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DEPARTMENT OF COMMERCE AND LABOR

BULLETIN
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

VOLUME 7
1911

WASHINGTON
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1911

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Vol. 7 No. 1

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NOTE ON THE TEMPERATURE SCALE BETWEEN 100° AND 500° C

By C. W. Waidner and G. K. Burgess

At the present time the standard scale of temperatures in the interval 0° to 100° C is that defined in a resolution of the International Committee on Weights and Measures, namely, that of the constant-volume hydrogen thermometer.[1] Above 100° temperature measurements have been made with air, hydrogen, and nitrogen thermometers, and in recent years there seems to be a preference to work with the constant-volume nitrogen thermometer.

In a previous paper[2] the authors determined the melting and freezing points of a number of metals on the temperature scale defined by the platinum resistance thermometer calibrated in ice, steam, and sulphur vapor (444°.70 on the constant-volume nitrogen thermometer). In order to throw further light on the probable accuracy of the temperature scale so defined, in the interval 100° to 500° C, the authors have made some further measurements by the same method on the boiling points of naphthaline and benzophenone, which temperatures have been determined by a number of observers using both platinum and gas thermometers.

Four thermometers were used, made of different sizes of pure platinum wire from Heraeus and from Johnson, Matthey & Co., and having fundamental intervals ranging from 1.1 to 10.6 ohms. Three of these thermometers were used both as Siemens three-lead compensated and as four-lead potential terminal thermometers. The apparatus and methods are fully described in the previous paper.

The boiling points were determined with the sulphur-boiling apparatus, using glass tubes about 4.5 cm diameter and 45 cm long, furnished with a side condenser tube with inlet near the top, and the thermometer was shielded by an aluminium cone in exactly the same way as in sulphur. With this shield omitted, the thermometer readings were about 0°.08 low in naphthaline and 0°.35 low in benzophenone. Raising the thermometer 6 cm produced a lowering in temperature of less than 0°.02.

---

[1] References will be found at the end of the paper.

Besides the boiling-point determinations, a few measurements were also taken of the freezing points of tin, cadmium, and zinc to compare with the previous work. The results are given in Tables I and II. It will be seen that the freezing points newly determined are practically identical with those previously found by the authors, showing that the temperature scale of the present work is in agreement with that of the previous investigation.

TABLE I

Determinations of Boiling Points of Naphthaline and Benzophenone, Wheatstone Bridge and Potentiometer Methods

On Ice, Steam, Sulphur (=444.70) Scale of Platinum Resistance Thermometer

1. BOILING POINT OF NAPHTHALINE

Date 1910	Therm. No.	Method	Observed Resistance	R_0	F. I.	δ	Obs. Pt. Temp. $-Pt_2$.	Obs. Temp. of Boiling	Reduced Barometer	Boiling Point	Substance
3.29	1787 B	W. B.	20.8987	11.5263	4.3787	1.513	214.04	217.93	758.34	218.03	K
3.30	"	"	20.8953	"	"	"	213.97	217.85	756.74	218.04	K
4.19	"	"	20.8572	11.5262	4.3784	"	213.11	216.95	742.11	217.99	K 1 recrys
3.29	1787 C	W. B.	6.33964	3.47222	1.33965	1.505	214.04	217.91	757.99	218.03	K
3.30	"	"	6.33815	"	"	"	213.93	217.79	756.54	217.99	K
4.19	"	"	6.32746	3.47219	1.33975	"	213.12	216.94	742.03	217.98	K 1 recrys
3.29	1787 D	W. B.	51.6262	28.7925	10.6674	1.500	214.05	217.90	757.98	218.02	K
4.15	"	"	51.5562	28.7923	"	"	213.40	217.22	747.06	217.97	K 1 recrys
4.19	"	"	51.5307	28.7921	10.6675	"	213.16	216.97	742.49	217.99	K 1 recrys
4.28	"	P. T.	51.5706	28.7801	10.6623	"	213.75	217.59	753.15	217.99	K 1 recrys
4.15	1787 F	W. B.	5.27421	2.89055	1.11702	1.502	213.39	217.21	746.89	217.97	K 1 recrys
4.19	"	"	5.27122	"	"	"	213.13	216.94	742.33	217.97	K 1 recrys
4.28	"	P. T.	5.32087	2.93016	1.11854	1.500	213.73	217.57	752.85	217.98	K 1 recrys
"	"	"	5.32080	"	"	"	"	"	752.94	217.98	K 1 recrys
				Boiling Point of Naphthaline, Kahlbaum							**$218.02 \pm 0.01_4$**
				" " " " " 1 recrys							**$217.98 \pm 0.01_1$**

Some measurements made in 1907 by one of the authors also gave for Kahlbaum naphthaline boiling point 218°.02.

TABLE I—Continued.

Determinations of Boiling Points of Naphthaline and Benzophenone, Wheatstone Bridge and Potentiometer Methods—Continued.

2. BOILING POINT OF BENZOPHENONE

Date 1910	Therm. No.	Method	Observed Resistance	R_o	F. I.	δ	Obs. Pt. Temp. $-Pt_b$	Obs. Temp. of Boiling	Reduced Barometer	Boiling Point	Substance
4.6	1787 B	W. B.	24.4616	11.5263	4.3787	1.513	295.41	304.85	741.14	306.04	K
4.8	"	"	24.4884	"	"	"	296.03	305.53	751.20	306.08	K
4.14	"	"	24.4989	"	"	"	296.27	305.79	752.31	306.27	M 2 recrys
5.3	"	P. T.	24.4585	11.50955	4.3739	1.511	295.05	305.54	751.86	306.05	K recrys
4.6	1787 C	W. B.	7.42996	3.47222	1.39965	1.505	295.43	304.83	742.01	306.02	K
4.8	"	"	7.43603	"	"	"	295.89	305.32	751.99	305.83	K
4.8	1787 D	W. B.	60.3668	28.7925	10.6674	1.500	295.99	305.40	750.83	305.98	K
"	"	"	60.3716	"	"	"	296.03	305.43	750.81	306.02	K
4.14	"	"	60.3943	"	"	"	296.25	305.68	752.58	306.15	M 2 recrys
4.8	1787 F	W. B.	6.19652	2.89056	1.11703	1.502	295.96	305.38	750.92	305.95	K
4.14	"	"	6.19967	"	"	"	296.24	305.68	752.15	306.17	M 2 recrys
5.3	"	P. T.	6.24232	2.93016	1.11854	1.500	296.11	305.53	752.11	306.02	K recrys
				Boiling Point of Benzophenone (Kahlbaum)...............							306.00 ±0.053
				" " " " (Merck, 2 recrys)							306.2

K—Kahlbaum best grade, M—Merck, W. B.—Wheatstone Bridge with Siemens three lead thermometer, P. T.—potential terminal thermometer, R_o—resistance in ice, F. I.—fundamental interval, δ—constant in the formula $t-pt=\delta(t/100-1)t/100$.

TABLE II

Freezing Points of Tin, Cadmium, and Zinc

(To Connect With Temperature Scale of Previous Investigations)

1. FREEZING POINT OF TIN

Date 1910	Therm. No.	Method	Observed Resistance	R_o	F. I.	δ	Pt.	Freezing Point	Remarks
4.2	1787 F	W. B.	5,42965	2.89056	1.11703	1.502	227.31	231.91	K in Acheson graphite
4.27	"	P. T.	5.47290	2.93016	1.11854	1.500	227.32	231.91	" " " "
4.27	1787 D	P. T.	53.0111	28.7801	10.6623	1.500	227.25	231.84	" " "
			Range of previous observations (5 samples)..					231.94 231.83	K gave 231.92

TABLE II—Continued.

Freezing Points of Tin, Cadmium, and Zinc—Continued.

2. FREEZING POINT OF CADMIUM

Date 1910	Therm. No.	Method	Observed Resistance	R_0	F. I.	δ	Pt.	Freezing Point	Remarks
4.1	1787 C	W. B.	7.63076	3.47222	1.33965	1.505	310.42	321.10	K in Acheson graphite
"	1787 D	"	61.9000	28.7925	10.6674	1.500	310.36	321.00	" " " "
"	1787 F	"	6.35755	2.89056	1.11703	1.502	310.38	321.03	" " " "
			Range of previous observations (3 samples).					321.05 320.39	K gave 321.01

3. FREEZING POINT OF ZINC

4.28	1787 D	P. T.	71.3483	28.7801	10.6623	1.500	399.24	419.32	K in Dixon graphite, 1907 crucible
			Range of previous observations (5 samples).					419.46 419.25	K (3 samples) gave 419.37

For nomenclature, see Table I.

The reduction of the boiling points to normal pressure was made by means of formulæ satisfying the data both of Crafts and of Jaquerod and Wassmer.

For Naphthaline: $T_{760} = T_{obs} - 0.058 (H - 760)$.

For Benzophenone: $T_{760} = T_{obs} - 0.063 (H - 760)$.

The freezing points of 250 gram samples of the naphthaline and benzophenone used were found to be as follows:

Description	Freezing point of	
	Benzophenone	Naphthaline
From Kahlbaum	47.2	79.9
From Kahlbaum, recrystallized	47.2	80.4
From Merck, recrystallized	46.9	....

In Table III are collected the determinations of the boiling points of naphthaline and benzophenone as made by the various observers, and where possible the values have been reduced to the same basis, namely, to a scale on which the sulphur boiling point is 444°.70.

TABLE III

Boiling Points of Naphthaline and Benzophenone

Date	Observers	Method and Remarks	Naphthaline		Benzophenone	
			Observed	Reduced to S.B.P.=444.70	Observed	Reduced to S.B.P.=444.70
1883	Crafts[3]	Hydrogen thermometer	218.06	218.03	306.08	306.01
1891	Callendar and Griffiths.[4]	Pt. Therm. compared with c. p. air therm. (S. B. P.=444.53).	217.94	217.97	305.82	305.89
1891	Griffiths[5]	" " "	218.04	218.07	....	....
1904	Jaquerod and Wassmer.[6]	Hydrogen thermometer	217.68	(217.65)	305.44	(305.37)
1905	Travers and Gwyer[7]	Platinum thermometer (S. B. P.=444.53).	218.04	218.07	305.8	305.87
1908	Holborn and Henning[8].	Pt. therm. compared with c. v. nitrogen therm. (S.B.P.=445.00).	218.04	217.99	306.08	305.95
1910	Waidner and Burgess	Platinum thermometer (S. B. P.=444.70).	....	217.98	....	306.08
	Reduced Mean including all observations		217.97±0.08		305.85±0.16	
	" " excluding Jaquerod and Wassmer		218.02±0.04		305.95±0.05	

It will be seen that, with the exception of the determinations of Jaquerod and Wassmer, there is a close agreement. Their results may be low, owing to the fact that the condenser of their boiling apparatus was immediately above the gas thermometer bulb, which was not screened in any way against the cooling effects of condensation and radiation. It should also be noted that the volume of their gas thermometer bulb was only 66 cc, which is small for work of precision. Their results may be indirectly tested by assuming either of their boiling points as the third standardization temperature of a platinum thermometer and using the thermometer so calibrated to determine the sulphur boiling point. This procedure would give S. B. P. = 443°.0, a value 1°.5 lower than any determination, and for the constant δ of the platinum thermometer 1.40 instead of the usual 1.50 as found when S. B. P. = 444°.7 is used as the third standardization temperature.

In view of the very general use of the S. B. P. for the standardization of platinum thermometers, we have summarized in Table IV the results of the more important determinations of this temperature, and reduced them to the same basis, namely, that of the nitrogen constant-volume thermometer under a pressure of 1 meter of Hg at 0° C. The temperatures thus observed are obtained only under very definite experimental conditions which are described at length in the previous paper and elsewhere.

TABLE IV

Boiling Point of Sulphur by Gas Thermometer

Date	Observers	Method and Remarks	Observed S. B. P.	Reduced to const. vol. p_0 = 1 m Hg	Weight
1862	Regnault [9]	Constant volume; by interpolation	447.5	....	....
1891	Callendar and Griffiths.[4]	Constant pressure	444.53	444.74	2
1894	P. T. Reichsanstalt [10]	Constant volume, Wiebe and Böttcher scale.	444.5	444.5	1
1900	Chappuis and Harker [11]	Constant volume, corrected from 445.2	444.7	444.7	2
1901	Holborn [12]	Constant volume, extrapolated by Pt. resistance.	444.55	444.55	1
1903	Rothe [13]	Constant volume P. T. R. scale, Hg thermometers. (Thermocouples gave 445.0)	444.7	444.7	1
1909	Eumorfopoulos [14]	Constant pressure (Extrapolated for Hg expansion—443.7)	444.55	444.76	2
		Mean S. B. P.	....	444.68±0.08	

Messrs. Day and Sosman in a recent elaborate investigation [15] with a nitrogen constant-volume thermometer at high temperatures (400 to 1,550° C) have determined the freezing points of a number of metals, among them zinc and cadmium, by transferring from the gas scale with thermocouples. They find for the freezing point of zinc 418°.2, and for cadmium 320°.0, whereas the platinum resistance thermometer calibrated in ice, steam, and sulphur vapor (444°.70) gives 419°.4 and 321°.0 for zinc and cadmium, respectively, with a precision of 0°.05 C. The explanation of this difference is of great importance in accurately fixing the gas scale in the interval 100 to 500° C. If the freezing point of pure zinc is 418°.2, instead of 419°.4, then it would follow that the boiling point of sulphur must be 443°.5 instead of 444°.7, as found by a number of observers as above shown. (See Table IV.)

It should also be noted that the gas thermometer as used by Day and Sosman was adapted primarily to give the highest attainable accuracy for the higher range of temperatures; that is, above 1000° C, and that no measurements with the gas thermometer itself were made below 400°, nor did they consider their thermometer of sufficient sensitiveness in the lower temperature ranges to warrant a determination of its fundamental interval, 0–100° C.

Some further evidence on the accuracy of the gas scale that is defined by a platinum resistance thermometer calibrated in ice, steam, and sulphur (444°.70) is afforded by the comparison by Holborn and Henning of two platinum thermometers with a nitrogen thermometer in the interval 150° to 200° C. This work shows that the two scales so defined are in agreement to within a few hundredths of a degree. If the value usually assigned to the S. B. P. (444°.70) were over 1° high, then the scale defined by the platinum thermometer at 200° might be expected to be about 0°.2 high, whereas these observers find an extraordinarily close agreement between these two scales. It is also of interest to note that these observers give evidence that their gas thermometer agrees with Regnault's gas scale to within 0°.02 up to 230° C.

In view of the doubt, however, which is thrown on the present generally accepted value of the S. B. P. by the work of Day and Sosman, new determinations of this point made with the best modern facilities with apparatus designed for work in this range are much to be desired. Ordinarily one would conclude that the highly satisfactory agreement of the determinations by so many different observers, using different methods, as summarized in Table IV, would settle this point. A careful study of the gas thermometers and methods used, however, shows that they are open to many criticisms, and many refinements are now possible that were not available or whose importance was not so clearly recognized at the time these determinations were carried out. Thus, in some of these determinations air was used as the gas instead of nitrogen.

Glass or porcelain bulbs, so subject to changes in volume or to the emission or absorption of gases, were employed instead of metal bulbs. The coefficient of expansion of the bulb was not always determined with sufficient accuracy over the whole of the temperature range, and in some cases the coefficient used was found by an unwarranted extrapolation.

The use of a uniform scale by different experimenters is always most desirable. In view of the very general use of the value 444°.7 as the boiling point of sulphur on the scale of the constant volume gas thermometer, and in the light of the evidence that is now available, no change in this point is possible at this time. It is well to bear in mind, however, that the standard gas scale is not yet definitely and certainly fixed to an accuracy of 1° at 450° C.

The following fixed points represent the temperature scale which appears to best satisfy the available observations to 0°.1 for the reproduction of temperatures in the interval 100° to 500° C:

Freezing Points		Boiling Points	
Tin	231°.9 C	Naphthaline	218°.0 C
Cadmium	321 .0	Benzophenone	306 .0
Zinc	419 .4	Sulphur	444 .7

As these temperatures are on the constant volume scale, the reduction to the thermodynamic scale may be effected approximately if desired by adding 0°.2 at the sulphur point and a proportional amount at the lower temperatures, remembering that this correction is zero at 100° C. All of these substances may readily be obtained of sufficient purity to give a reproducibility of 0°.05 C from one sample to another.

WASHINGTON, May 13, 1910.

REFERENCES

1. Proces Verbeaux du Committee International des Poids et Mesures, Séance du 15 Octobre, 1887.
2. Waidner and Burgess: Platinum Resistance Thermometry at High Temperatures, Bull. Bureau of Standards, **6**, pp. 149–230; 1910.
3. J. M. Crafts: Les Mesures Thermometriques et la Determination des Points de Fusion et d'Ebullition. Bull. Soc. Chimique de Paris, **39**, pp. 277–289; 1883.
4. Callendar and Griffiths: On the Determination of the Boiling Point of Sulphur, and on a Method of Standardizing Platinum Resistance Thermometers by Reference to it. Phil. Trans., A **182**, pp. 119–157; 1891.
5. E. H. Griffiths (note to Ref. 4): Phil. Trans., A **182**, p. 151; 1891.
6. Jaquerod and Wassmer: Points d'Ebullition sous diverses Pressions de la Naphthaline, du Biphényle et de la Benzophènone, determiné au Moyen du Thermomètre à Hydrogène. Jl. de Chimie Phys., **2**, pp. 52–78; 1904.
7. Travers and Gwyer: Proc. Roy. Soc., **74**, p. 528; 1905.
8. Holborn and Henning: Über das Platinthermometer und den Sättigungsdruck des Wasserdampfes zwischen 50 und 200°. Ann. der Phys., **26**, pp. 833–883; 1908.
9. Regnault: Relation des Expériences, **2**, p. 526; 1862.
10. Thätigheit der P. T. Reichsanstalt: Zs. f. Instrumentenkunde, **14**, p. 304; 1894.
11. Chappuis and Harker: On a Comparison of Platinum and Gas Thermometers. Phil. Trans., A **194**, p. 37; 1900.
12. Holborn: Untersuchungen über Platinwiederstände und Petroläther Thermometer. Ann. der Phys., **6**, p. 242; 1901.
13. Rothe: Bestimmung des Schwefelsiedepunkts. Zs. f. Instrumentenkunde, **23**, p. 364; 1903.
14. Eumorfopoulos: The Boiling Point of Sulphur on the Constant Pressure Air Thermometer. Proc. Roy. Soc., **81**, p. 339; 1908.
    Callendar: Note on the Boiling Point of Sulphur. Proc. Roy. Soc., **81**, p. 363; 1908.
    Callendar: The Boiling Point of Sulphur corrected by Reference to New Observations on the Absolute Expansion of Mercury. Proc. Roy. Soc., **83**, p. 103; 1909.
15. Day and Sosman: The Nitrogen Thermometer from Zinc to Palladium. Am. Jl. Sci., **29**, pp. 93–161; 1910.

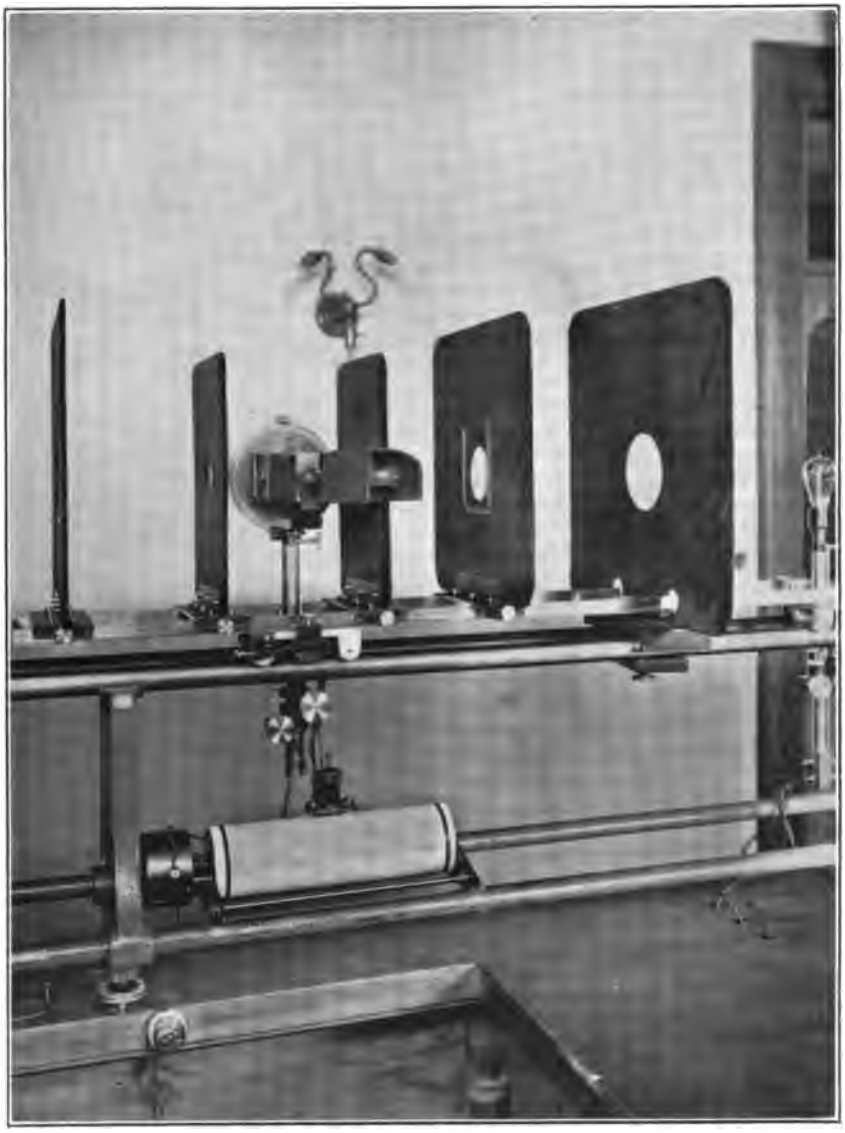

Fig. 1.—*Recording Apparatus Mounted on Photometer Frame.*

A NEW FORM OF DIRECT-READING CANDLEPOWER SCALE AND RECORDING DEVICE FOR PRECISION PHOTOMETERS

By George W. Middlekauff

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I. INTRODUCTION

The new form of candlepower scale herein described was designed for use in the precision photometric work of the Bureau of Standards, and is the result of an attempt to combine the direct-reading feature of the ordinary commercial photometer candlepower scale with the accuracy possible in the use of the precision photometer. It is intended to be used in connection with an automatic recording device, also designed for use in the Bureau of Standards, and described in the transactions of A. I. E. E.[1] The automatic recorder eliminates the labor and possible errors of reading and recording the great number of settings made in a series of photometric measurements, while the direct-reading scale described below eliminates the labor and possibilities of error involved in the considerable computations heretofore necessary in finding the values of the lamps in terms of the mean of a group of standards.

II. THE PHOTOMETRIC APPARATUS AND THE DETERMINATION OF CANDLEPOWER

1. THE PRECISION PHOTOMETER AND METHOD OF MEASUREMENT

The precision work of the bureau in the photometry of electric incandescent lamps is done on a standard photometer of the Reichsanstalt pattern, supplied with a Lummer-Brodhun contrast screen, and the measurements are made by the substitution method; that is, the standards and the lamps to be compared with them are placed, in turn, in the socket near the left end of the bar, or test side, and are balanced against a comparison lamp placed near the right end, or comparison side. In order to eliminate all variables on the comparison side, and thus carry out the substitution method more perfectly, the two separate carriages supporting the comparison lamp and the photometer screen, respectively, are connected rigidly by means of adjustable rods (which are set before measurements are made), in order to maintain a constant distance between the comparison lamp and the screen, this distance being so determined as to throw the balance for a lamp of given candlepower at or near some desired distance from the lamp. The illumination of the comparison side of the screen is thus kept constant throughout the set of measurements, and the candlepowers of the lamps compared are directly proportional to the squares of their respective distances from the screen when it is set at photometric balance.

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[1] In a paper on "Carbon Filament Lamps as Photometric Standards," presented by E. B. Rosa and G. W. Middlekauff at the Twenty-seventh Annual Convention, June 28–July 1, 1910.

2. OLD METHOD OF READING AND RECORDING SETTINGS

Before the introduction of this new device the photometer settings were read by the observer from a centimeter scale graduated on the bar, and the readings were recorded by hand in a book provided for the purpose. From five to fifteen settings and corresponding readings of the scale, according to their range, were made on each lamp, thus making it necessary for the observer to record from two to even as many as five times during the measurement of each lamp, it being impossible to retain in mind more than about three readings at a time for correct recording.

This method of reading and recording settings is objectionable, because it consumes considerable time and involves the liability of error, both in reading and in recording, besides unnecessarily fatiguing the eye by alternate reading of photometer screen and scale.

3. OLD METHOD OF COMPUTING CANDLEPOWER

The readings having been recorded and the mean reading found for each lamp, it was then necessary, in order to find the candlepower values, to perform a tedious set of computations as shown by the following formula:

$$X = \frac{A+B+C+D+E+F}{a^2+b^2+c^2+d^2+e^2+f^2} \cdot x^2$$

where A, B, C, D, E, and F are the values of the six standards (it being desirable to use at least this number in every set of measurements) and X is the value of any lamp compared with them; while a, b, c, d, e, f, and x are the corresponding, respective, mean distances of the lamps as read from the centimeter scale on the bar. Although these computations were much abbreviated by the use of a set of tables prepared especially for this purpose, nevertheless the work was very tedious, involving, at the same time, the liability of error, thus making it absolutely necessary to have all the numerical work checked by a second computer whose task was equally laborious and required fully as much time as that of the first.

The ordinary direct-reading candlepower scale, such as used on commercial photometers, can not well be adapted to this class of work, because for precise measurement it is practically impossible to adjust the comparison lamp properly to "fit" the scale with the necessary accuracy; especially since, as stated above, it is desirable to employ at least six standards in the adjustment.

III. THE NEW APPARATUS

1. THE NEW FORM OF CANDLEPOWER SCALE

It occurred to the author that if the usual process of adjusting the comparison lamp to fit the candlepower scale were reversed and the scale were so constructed that it would adapt itself to the adjustment of the comparison lamp within certain reasonable limits the difficulty in using a commercial photometer scale for precision work could be avoided and the computations for candlepower eliminated. It was found that such a scale could be computed and constricted in a very simple and satisfactory manner, as explained below and as will be understood by referring to the accompanying Fig. 2.

The scale proper is the rectangular area *ABDC* and is calculated on the basis that a 16-cp lamp is to be measured with the photometer screen at a distance of approximately 120 cm from the lamp, a range of 6 cm either side of 120 cm being allowed in the construction of the scale. The sides *AB* and *CD* of the rectangle are two ordinary linear candlepower scales calculated to suit the arrangement of the photometer as described in the second paragraph above for two different adjustments of the comparison lamp, and the points of graduation were determined by means of the formula

$$\frac{x^2}{a^2}=\frac{X}{16} \quad \text{or} \quad x=\frac{a}{4}\sqrt{X}$$

where a is the distance of the 16-cp point of graduation from the lamp (or zero of the scale), being 126 cm for the scale *AB* and 114 cm for the scale *CD*, and x is the corresponding distance of any other cp point X on the scale that is being calculated. The rectangle was made 30 cm in length so as to include the candlepower points most commonly required in standardizing work, these being indicated along the sides *AB* and *CD*. The balance for lamps having values above or below those indicated, for instance, 32-cp or 8-cp lamps, may be thrown within this range by means of rotating sectored disks placed on the proper side of the photometer screen or, in the case of low-intensity lamps, by a method described later. The diagonal lines, all of which are

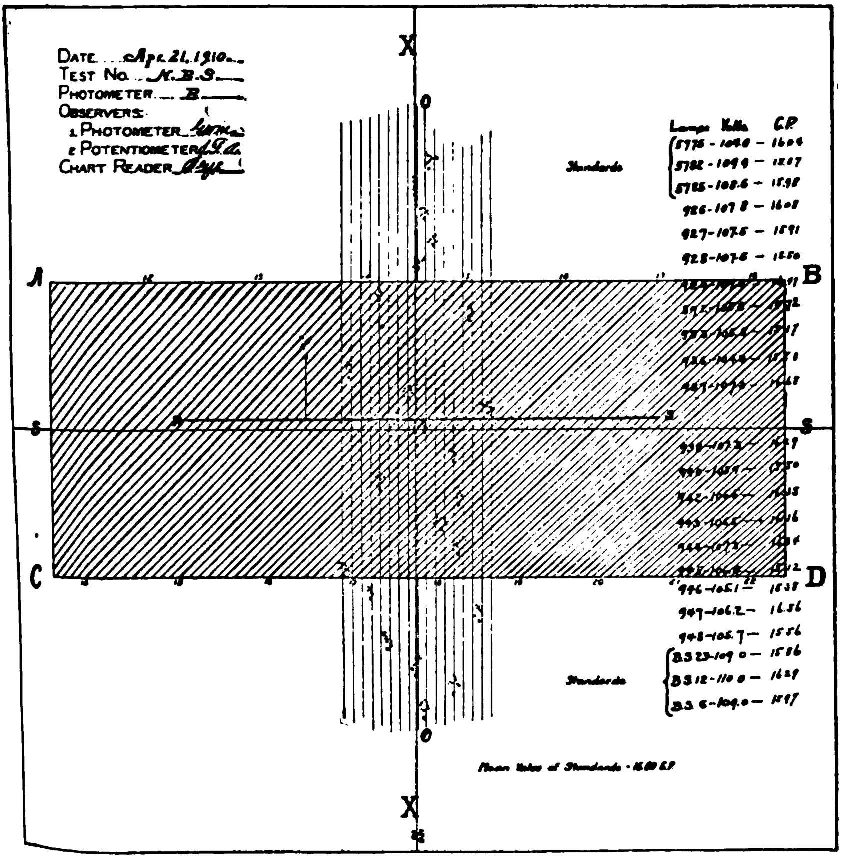


Fig. 2.—*Candlepower Scale and Record Chart. Comparison Lamp Movable with Photometer Screen*

straight, join the corresponding one-tenth candlepower points of graduation in the two scales; and since these two scales are divided proportionately, all the diagonal lines must converge toward a common point in a line drawn through zero and perpendicular to both scales. The slope of this system of lines depends upon the distance between *AB* and *CD*, which may be chosen arbitrarily. In order to prevent too much crowding of the diagonal lines on the one hand and too large a rectangle on the other, the 16-cp line was drawn so as to make an angle of 45° with the sides *AB* and *CD*, the other lines of the system being drawn in their proper directions accordingly. The rectangle thus becomes 12 cm in width and, as stated above, it was arbitrarily made 30 cm in length.

Now, any line drawn across the diagonal lines and parallel to the length of the rectangle will be divided in exactly the same proportion as *AB* and *CD* and will, therefore, be a candlepower scale also. Hence this rectangle includes an indefinite number of linear candlepower scales and corresponding to any fixed adjustment of the comparison lamp that will throw the 16-cp balance at any point within the 12-cm range between the limits of the 16-cp diagonal line (*i. e.*, between 114 cm and 126 cm from the lamp), there will be, in the rectangle, a linear scale that will exactly fit the comparison lamp adjustment. The method of determining the exact position of the proper linear scale for any given adjustment will be fully explained below.

Two important reference lines *XX* and *SS* are drawn across the figure perpendicular to each other and to the sides of the rectangle, intersecting the 16-cp diagonal line at its middle point, which is also the middle point of the rectangle and is at exactly 120 cm from the lamp located at zero of the scale. Hereafter, the line *XX* will be called the "index line," being the line by which the diagonal scale is set at its proper distance from the lamp mounted at zero on the photometer bar, and the line *SS* will be called the "standard scale," as it is the linear scale on which 16 cp falls at exactly 120 cm from the lamp, this being the distance adopted in the bureau's practice as standard in the comparison of electric incandescent lamps of 16-cp intensity, the illumination of the photometer screen under these conditions being approximately one foot-candle.

2. THE PAPER RECORD SHEET

The rectangular figure, as described above, was very accurately drawn just double the required dimensions, and after being photographed down to the correct size, it was transferred to a copperplate etching from which it was printed, in olive green, on sheets of white paper about 35 cm square, one of these sheets being intended for each separate set of lamps photometered.

The paper used for this purpose was specially prepared to better withstand changes in dimension due to ordinary variations in atmospheric humidity. As a further precaution, the longer dimension of the rectangle, which is the important one to keep constant, was printed parallel to the machine direction of the paper; that is, to the direction in which it is the least affected by changes in humidity.

By actual test made at the bureau on several samples of the paper about 35 cm square, it was found that under an increase in humidity from "dry" to saturated, the average total increase in dimension in the machine direction of the paper was about 0.9 mm, while at right angles to this direction the average total increase was 5.7 mm.

Now, any approximately uniform change in the width of the rectangle requires no consideration, because it has no effect upon the accuracy of the scale. It simply changes the slope of the lines, as a system, without altering the proportion in which they divide any line drawn across them and parallel to the length of the rectangle. A change of 0.9 mm in the length of the rectangle, however, means a change of 0.45 mm in the relative position of a point at the end of the scale with reference to the index line which is always placed at its proper distance from the lamp photometered; and 0.45 mm change in length is equivalent to about 0.01 candle, or 0.08 of 1 per cent of 12 cp at the lower end of the scale, and to about 0.015 candle, or 0.07 of 1 per cent of 22 cp at the upper end. Therefore, the maximum error possible in candlepower readings under the most unfavorable conditions can not be as much as 0.1 of 1 per cent. Indeed, numerous measurements of the length of the scale at various times and under various degrees of atmospheric humidity have failed to show any variation large enough to be detected by means of a millimeter scale. Hence with the candlepower scale printed parallel to the machine direction, on paper of this kind, no appreciable error is introduced in candlepower readings as a result of any possible variations in atmospheric humidity, and especially is this true if all the settings are made, as they should be, as near the central portion of the paper as possible.

3. THE RECORDING DEVICE

While observations are made, one of the printed sheets of paper may be held under the photometer carriage by means of a flat table, movable at right angles to the photometer axis, or, as is done at the bureau, it may be wrapped on a cylinder (Fig. 1) whose axis is parallel to the photometer bar. By pressing a key located on the photometer carriage the observer prints on the paper a record dot for each setting as it is made, this being done by means of a printing electro-magnet suspended from the photometer carriage by a metal rod, the magnet being provided with two revolving spools carrying a carbon ribbon between the printing point and the sheet on the cylinder. The cylinder rests on the frame of the photometer bench and is turned on its axis by an electrically driven clock connected to it by means of a friction clutch which permits the cylinder to be turned by hand, if desired, without disturbing the clock. The clock and the printing magnet are operated in series by a battery of four storage cells, the magnet printing when the key is closed, the clock turning the cylinder a half mm when the key opens. The record dots are thus prevented from falling together, and by their relative positions they show the order in which the settings are made.

IV. THE NEW APPARATUS IN PRACTICAL USE

1. THE NECESSARY ADJUSTMENTS

The complete adjustment of the apparatus preliminary to making a series of measurements is simply as follows: The photometer carriage is set with the test side of the screen at 120 cm on the bar and the paper record sheet is wrapped on the cylinder and clamped, the index line having been previously placed immediately under the printing point and overlapped at its opposite ends. Then with a standard 16-cp lamp, burning at its correct voltage, in the socket at zero on the test side, and the comparison lamp burning at the proper voltage to match the standard in color, the rods connecting the photometer and comparison lamp carriages are adjusted so as to throw the intensity balance anywhere within 6 cm either side of the index line, and the apparatus is ready for making measurements. The only adjustment requiring any degree of care is that of placing the index line at its proper distance of 120 cm from the lamp to be photometered.

2. RECORDING THE SETTINGS

Settings are now made on the standard lamp, and are recorded by a corresponding group of dots printed near the top of the sheet. The standard is then removed, the cylinder is turned by hand a distance sufficient to separate the group of dots just made from those to follow, and other standards, if desired, or lamps to be standardized are placed in turn in the socket and for each lamp the settings are recorded by a corresponding group of dots, as before. The record is thus continued down the length of the paper until all the lamps of the set are photometered.

A photographic reproduction of a completed record sheet, or chart, of a series of measurements actually made in this manner on a set of six standards and seventeen lamps compared with them is shown in Fig. 2, the lamps under measurement being part of a lot designated as "N. B. S." lamps. In the three columns of figures along the right margin are given the numbers of the lamps in the order they were photometered and recorded by the dots, together with their respective voltages and corresponding candlepower values. The cross mark under each group of dots indicates the average position of the individual dots of the group, this position being located usually by estimation. The candlepower values of this set were read from the linear scale *RS* whose correct position was determined in the manner described below. This will be referred to hereafter as the "record scale," being that scale which fits the adjustment of the apparatus and therefore of the record printed on the sheet.

3. READING THE RECORD

With the chart on a drawing board and by means of a T square with its edge parallel to the index line, preliminary relative candlepower values of the six standards were read from the standard scale and each reading was recorded by a mark on this scale as shown.

These readings, in the order of the record of the standards, were 16.15, 15.98, 16.09, 15.97, 16.40, and 16.08 cp, respectively, their mean being 16.11 cp. As the true mean value of these six standards happened to be 16.00 cp, it is evident that the linear record scale *RS* must lie above the standard scale and at such a distance from it that the 16.00-cp point on *RS* falls on the line *OO* which was drawn (by means of the T square) perpendicular to the standard scale at its 16.11-cp point.

The simplest method of determining the proper position for the record scale is to consider the line *OO* as a linear candlepower scale and draw *RS* intersecting it at the point where the reading is the mean true value of the standards; that is, at 16.00 cp for this particular case. No appreciable error is introduced by considering the line *OO* as a candlepower scale, because at this part of the rectangle the diagonal lines are so nearly parallel to one another that, for practical purposes, we may consider *OO* divided in the same proportion as the standard scale and the reading at the intersection of *OO* and the record scale will be the same on both.

With the record scale properly drawn, it becomes a simple matter (by means of the T square) to read off the correct values in candlepower directly and as rapidly as it is possible to set the edge of the T square over the centers of the various groups of record dots. It has been found by experience, however, that, instead of simply reading off the values in this manner, it is better practice to draw a vertical line through the intersection of each diagonal line with the record scale, a sufficient number of such vertical one-tenth candle lines being drawn to include all the groups of dots close together in value. In the case of any group that may be separated from the others, as, for instance, the one corresponding to lamp No. 892, the eighth in the set, it is better to draw a line directly from the center of the group to the scale. The advantage of having these lines on the chart is that the values can be more easily and more accurately read; and especially that the record is thus made more complete and permanent, permitting it to be checked in a few moments by a second reader.

The values of all lamps of the set, including the standards, are read off to the nearest 0.01 candle and written along the margin of the chart. If the linear record scale has been carefully drawn at the proper distance from the standard scale, the mean of the standards, as read from it, will equal the true value to within 0.01 candle. Experience has shown that it is very seldom necessary to apply a correction to the final mean reading of the standards, showing that with ordinary care the record scale can be drawn with all the precision necessary. If, however, on account of inaccuracy in drawing the record scale, the mean reading of the standards should differ from the true value by a few hundredths of a candle, the difference is applied as a percentage correction to each reading in the set, being added or subtracted according as the mean of the standards reads too low or too high. Usually all the lamps of a set are so nearly equal in value as to permit a constant correction to each reading without introducing an error due to a lack of proportionality.

The true candlepower values of the individual standards used in the set given in Fig. 2 were, in the order recorded, 16.00, 15.90, 15.98, 15.82, 16.33, and 15.96, respectively. A comparison of these values with those read from the scale and written on the chart gives a fair indication of the accuracy of the settings made on the photometer.

4. USE OF SECTORED DISKS AND COLOR-ABSORBING SCREENS

When it becomes necessary to use rotating sectored disks to make the record of any lamp fall on the sheet, the final value of such lamp is determined by simply applying the disk factor in the proper manner to the value as read from the scale. For lamps of lower intensity than the standards, a balance at the desired place on the sheet may be obtained by placing the disk either on the comparison side when settings are made on the low-intensity lamps or on the test side when settings are made on the standards. In the former case the illumination of the photometer screen is not the same throughout the comparison, and there may be a possibility of error due to the Purkinje effect. In the latter case the illumination of the screen is the same throughout the comparison, but it can not be greater than that produced by the lamp of the lowest intensity, and may therefore be rather weak for accurate measurement. Although this latter method of measurement is preferable to the former when low-intensity lamps are measured, yet it is inferior to a method that will be given when the sectional candlepower scale is described below.

For the most accurate measurement it is an advantage to work with a color match. When high-efficiency lamps, such as tantalums and tungstens, or carbon lamps operated at high efficiency, are compared with 4-wpc standards, a color match can be obtained by the use of carefully calibrated red or blue glass screens of the required density on the proper side of the photometer. With the comparison lamp set for 4-wpc color match with the standards, the blue glass is inserted on the comparison side, or the red glass on the test side when the high-efficiency lamps are photometered. Or, with the comparison lamp set for color match with the high-efficiency lamps, the blue glass is inserted on the test side when settings are made on the standards. On the other hand, when lamps of low efficiency are compared with 4-wpc standards a match in color is obtained by reversing this process. Whenever a color screen is used on the comparison side in either case, it should be replaced by a rotating sectored disk having approximately the same transmission coefficient as itself when the standards or other lamps of the set not requiring its use are photometered, in order to maintain the illumination of the photometer screen constant throughout the set of measurements. In any of these cases the transmission coefficients of the glass and of the disks used must be applied as factors in the proper manner to the candlepower values as read from the scale.

5. COMPARISON OF LAMPS WITH STANDARD ILLUMINATION OF THE SCREEN

It may be desirable, and is no doubt preferable, to compare low intensity lamps, such as 8 cp and 4 cp, with 16-cp standards with the illumination of the screen constant throughout the comparison and approximately 1 foot-candle as standard, rather than with lower illumination, as is necessary by the method described in the paragraph on the use of rotating sectored disks.

This may be accomplished by two different methods. By the first method all lamps compared are placed, in succession, at zero on the bar and settings are made without the use of sectored disks. With the apparatus so adjusted as to throw the balance for the 16-cp standards at 120 cm, all the settings are made with standard illumination of the screen, but they extend over a range of at least 60 cm, falling at 120 cm on the bar for the standards and at 60 cm for the 4-cp lamps. This method is objectionable because it may be inconvenient, on account of some accessory part of the apparatus, to move the photometer carriage over so great range, and especially because, if the settings are to be automatically recorded, a continuous record sheet and scale of the required length (that is, of at least 70 cm) would possibly make the printed scale unreliable on account of changes in its length due to variations in atmospheric humidity, and besides the sheet would be very large and unwieldy for handling and filing purposes.

By the second method the settings are also made without the use of sectored disks and the apparatus is adjusted in the same manner as in the first method, but the lamps of low intensity are placed, in succession, at such points on the photometer bar that the settings fall at approximately 120 cm from zero for every lamp. For instance, an 8-cp lamp placed at 35 cm, or a 4-cp lamp at 60 cm, on the bar produces approximately the same illumination on the photometer screen at 120 cm as a 16-cp lamp placed at zero. With the lamps thus placed, in succession, all settings are made with standard illumination of the screen and near 120 cm on the bar, but the scale, as described above, will not serve for the correct reading of the candlepower of the lamps not placed at zero. Fortunately, however, the scale will adapt itself perfectly to the new conditions if it is divided into sections as shown in Fig. 3 and as described below.

V. THE NEW SCALE IN SECTIONAL FORM

1. METHOD OF CONSTRUCTION

In order to understand clearly how the scale may be divided into sections so as to make it direct reading for lamps of such intensities as those mentioned above, when placed at the points indicated, let us suppose that the lamps are all placed at first, in succession, at zero, and that a record of the settings made on them is printed by dots on a continuous scale of the required length. The record of the 4 cp, the 8 cp, and the 16 cp lamps will then fall at 60 cm, 85 cm, and 120 cm, respectively, from zero. Now suppose that an index line is drawn across the scale at each of these three points and that the scale is divided into three sections, each containing an index line and the record dots corresponding to one of the lamps, these being at or near the middle of the section. If the 8 cp and the 4 cp lamps are now moved to the points mentioned above; that is, to 35 cm and 60 cm, respectively, from zero on the bar, and if with each lamp the section on which the record of its settings appears is moved forward by the same amount as the lamp, it is evident that the index lines of all three sections will fall together and that the record dots will occupy exactly the same relative positions with respect to one another as if they had been made with

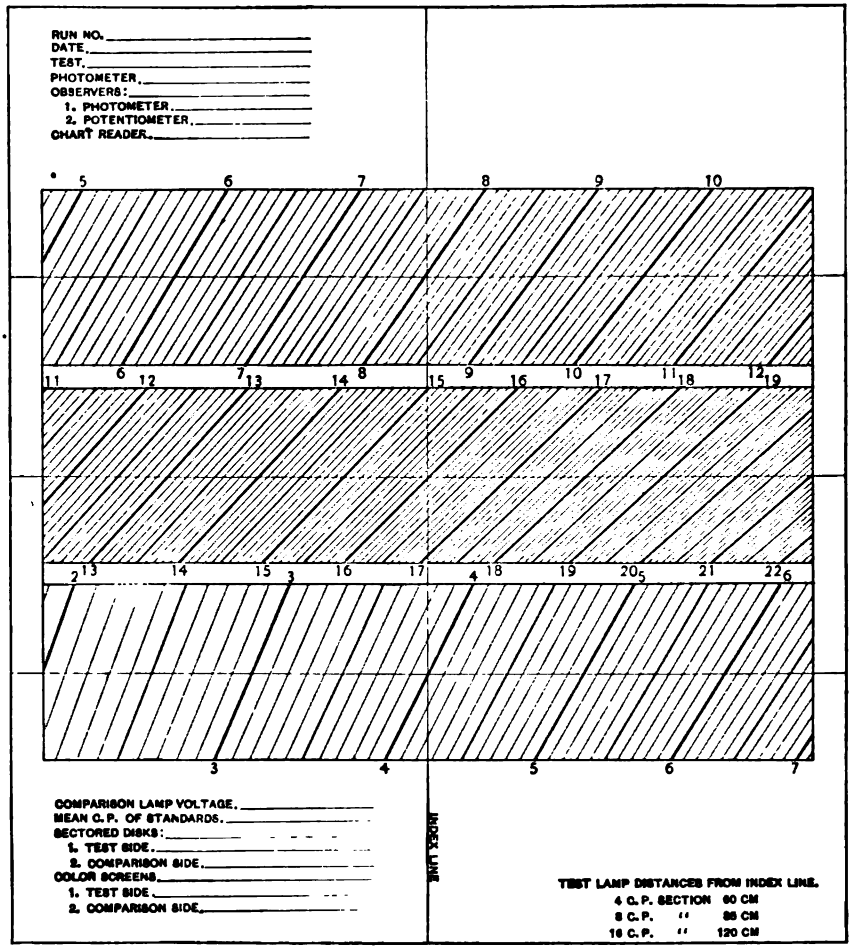


Fig. 3.—*Candlepower Scale in Sectional Form. Comparison Lamp Movable with Photometer Screen. Test Lamps may be Placed Successively at Different Points on the Photometer Bar.*

the lamps located thus at three different points on the photometer bar. Hence, if these three sections (which will be referred to hereafter as "the 4-cp section," "the 8-cp section," and "the 16-cp, or standard, section," respectively) are placed, not superposed, but parallel and adjacent to one another as indicated in Fig. 3, with the index lines end to end as shown, thus forming a "sectional candlepower scale," which is then printed on the record sheet, the values of all the lamps of all three intensities may be read off directly in candlepower, each from its corresponding section of the scale.

As it will be seen, these three sections include all values continuously from 2 to 22 candles, there being a repetition in the region of 5 and 6 cp. This repetition was made purposely, in order to throw the 5-cp point nearer the middle of the scale than it falls on the 8-cp section, this being desirable because the bureau at present has more or less standardizing to do in this region of intensity and the record dots are thus at a point on the scale where a change in the length of the scale would be less liable to produce an appreciable error in the reading. The 16-cp, or standard, section was drawn in the middle portion of the sectional scale in order that it may lie between the two parts of the record of the settings on the standards which usually appear at the top and bottom of the sheet; and also for the reason that the greater number of lamps intended for standards are of such intensities as are read from this section. With a centimeter space allowed between adjoining sections, the over-all dimensions of this sectional scale are 35 cm in length by 26 cm in width. The individual sections are 8 cm in width, this being found by experience with the scale shown in Fig. 2 to be ample for all practical purposes. This scale is now being engraved and printed for the bureau on record sheets 40 cm by 37.5 cm, the latter dimension being in the direction of the length of the scale, and it will be used whenever lamps of low intensity are to be photometered.

2. ADAPTATION TO THE PRINTED RECORD

It is evident that the record scale should appear on every section and at exactly the same distance from the standard scale on each section, as would be the case were the sections together in one continuous diagonal scale. It is first located on the standard section, in the usual manner, and then drawn at the same relative position on the other two sections. This drawing is quickly and accurately done by means of (what we shall call) a "triple right-angle sliding index" (shown in Fig. 6), having the three corresponding edges, which are perpendicular to the edge of the T square, exactly 9 cm apart, so that when the middle edge is placed on the standard scale of the 16-cp section, the other two edges will fall exactly on the standard scale lines, respectively, of the other two sections. Hence, when it is correctly placed to draw the record scale on the 16-cp section, it is at the same time in correct position to draw the corresponding line on each of the other two sections, and all three lines may be drawn without moving the index.

Although corresponding to each section of the scale, there is a definite distance (which for the sake of brevity will be referred to as its "lamp distance") at which the lamp must be placed with respect to the common index line on the sectional scale, if its value is to be read off directly, nevertheless, the scale as a whole readily adapts itself to any other lamp distance than those specified. For example, suppose that a lamp is for some reason at a distance of 65 cm from the common index line. Its value is read from the 4-cp section, but at a point 5 cm higher on the scale than is represented by the record. This is for the reason that had the lamp been placed at the exact lamp distance for the 4-cp section (that is, at 60 cm) instead of at 65 cm, the record would have fallen just 5 cm higher on the scale, in which case the reading would have been direct. Supposing, for a second example, that the lamp distance is 75 cm; the value is then read from the 8-cp section (whose lamp distance is 85 cm) at a point 10 cm lower on the scale than is represented by the record. These higher or lower readings are taken by means of a centimeter scale graduated on the edges of the triple index, as shown in Fig. 6.

Another condition, which is equivalent to placing every lamp of a set at an incorrect distance in the same direction by the same amount, exists when the common index line on the record sheet is not exactly at 120 cm from zero of the scale when the settings are recorded. The values may be read off correctly in the same manner as above by allowing the correction in distance when reading the scale. For instance, if the common index line is set at

121 cm from zero, then all the record dots are 1 cm too low and hence each reading, to make it direct in candlepower, should be taken just 1 cm higher on the scale.

3. USE IN COMPARING FLAME AND ELECTRIC INCANDESCENT STANDARDS

A sectional scale, such as just described, is useful in the comparison of a flame standard with a standard electric incandescent lamp, in which it is not only inconvenient but it is also undesirable to place the lamps compared, successively, at the same point, because the flame standard should be disturbed as little as possible during the comparison. In standardizing, or investigating, a 10-cp pentane lamp, for example, it is most convenient to have it located on a table at the end of the photometer bench with the flame in line with the photometer axis and at a distance of about 30 cm from the zero point; and to have the incandescent lamp placed, in turn, at some point on the photometer bar, the light from the pentane lamp being screened off while the incandescent lamp is measured. In this way the flame standard need not be disturbed at any time during the comparison.

As it is desirable to photometer the pentane lamp at the standard distance of 100 cm, as adopted by the London Gas Referees, the scale to be used in such comparisons should be constructed on the basis that 10 cp falls at exactly 100 cm from zero, whereas on the scale shown in Figs. 2 and 3 it falls at approximately 95 cm from zero. The distance between the index lines on the undivided scale should, of course, be the same as the distance between the points at which the lamps compared are located when each, in its turn, is photometered.

4. AS CONSTRUCTED FOR USE WITH AN INTEGRATING PHOTOMETER

In the case of some instruments, such as the Matthews integrating photometer and the Ulbricht sphere, the test lamp and the photometer screen remain stationary, the settings being made by varying the distance of the comparison lamp. The sectional scale for this arrangement is constructed on the same principle as the one already described, but the equation used in computing the candlepower points is $x = 4a\sqrt{\frac{1}{X}}$ since here the candlepower X, of the test lamp varies inversely as the square of the distance x, of the comparison lamp. In this case only one section of the scale is useful at any given position of the cylinder on the photometer bench. For lamps higher or lower in candlepower the cylinder is moved the proper direction to a new position bringing another section of the scale into use. The scale is properly located by first making an approximate setting on a standard then adjusting the position of the cylinder so that the middle of the record sheet comes under the printing point of the magnet (suspended from the comparison-lamp carriage) or, if possible, so that the common index line falls at a distance from the screen exactly equal to the lamp distance corresponding to one of the sections. But should the distance of the index line differ from the lamp distance by a known amount, the allowance is made as described above when reading the scale.

VI. THE SCALE ADAPTED TO PHOTOMETERS HAVING BOTH LAMPS STATIONARY

1. THEORETICAL DISCUSSION

The candlepower scale in the forms thus far described is adaptable only to such photometers as have either the test lamp or the comparison lamp at a constant distance from the photometer screen. In these forms all the candlepower lines are theoretically straight and join corresponding points of division in two linear scales forming the upper and lower sides, respectively, of the rectangle. It will now be shown that the same method may be used in constructing the scale in a form adaptable to photometers having both lamps stationary.

Let C and T be the values of the comparison lamp and the test lamp, respectively, D, the constant distance between them, and x the distance of the screen from the test lamp. Then for photometric balance

$$\frac{T}{C}=\frac{x^2}{(D-x)^2} \tag{1}$$

from which

$$x=\frac{D}{1+\sqrt{\frac{C}{T}}} \tag{2}$$

In order to plot the locus of the balance point of the photometer screen corresponding to a given value of T, while the value of the comparison lamp is varied continuously, let the values of x be distances measured on the X-axis of coordinates, and let distances to be measured on the Y-axis be represented by

$$y = \frac{D}{1+\sqrt{\frac{T_0}{C}}} \tag{3}$$

where C has the same value as in equation (2), while T_0 is a particular value of T in the same equation; that is, the Y-axis is regarded as a linear candlepower scale for the comparison lamp when the test lamp is held constant at the value T_0.

In order that the locus of the point x, y may be plotted without a knowledge of the value of the comparison lamp, let C be eliminated by equating its value in equations (2) and (3), and thus obtain either

$$x = \frac{D(D-y)\sqrt{T}}{D\sqrt{T}+(\sqrt{T_0}-\sqrt{T})y} \tag{4}$$

or

$$y = \frac{D(D-x)\sqrt{T}}{D\sqrt{T}+(\sqrt{T_0}-\sqrt{T})x} \tag{5}$$

Now, in either equation $x=D$ when $y=o$, and vice versa, showing that the locus of the point intersects both axes at a distance D from the origin.

In the special case when $T=T_0$, both equations reduce to $x+y=D$, meaning that the locus for this case is a straight line. A further discussion of this case will be taken up below.

Since x and y are interchangeable in equations (4) and (5), it follows that the locus is symmetrical with respect to a line OE bisecting the right angle XOY between the axes. (See Fig. 4.)

If the coordinates are transformed so as to refer to a pair of axes parallel to the original ones by the substitution of $x'+a$, and $y'+a$ for x and y, respectively, in either (4) or (5), a being assumed equal to $\frac{D\sqrt{T}}{\sqrt{T}-\sqrt{T_0}}$, the equation reduces to

$$x'y' = a^2\sqrt{\frac{T_0}{T}} \tag{6}$$

Since the second member of equation (6) is a constant for any given values of T and T_0, the locus of the point x', y' is an equilateral hyperbola asymptotic to a pair of axes parallel to the XY axes, and at a distance of a from them, a of course being a different constant for each different curve of the system.

In the limiting cases when either T or T_0 is separately equal to o or ∞, the locus in each case degenerates into the axes of coordinates. When $T = T_0$ the locus consists of two parallel straight lines at an infinite distance, one on either side of the origin, and perpendicular to a line bisecting the angle between the axes. The former cases are of interest only from a mathematical standpoint; the latter, however, is important because under this condition one branch of the locus, referred to above, becomes (as will be seen later) the reference line of the system when the lines are drawn as actually used in the scale and the coordinates are referred to the XY axes as in equations (4) and (5).

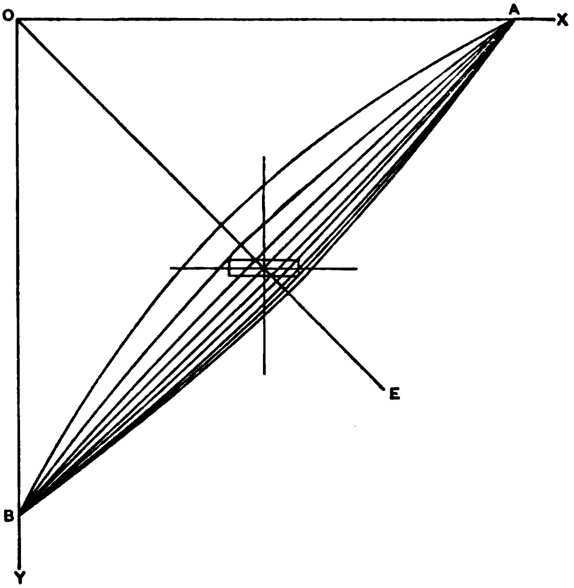


Fig. 4.—*System of Candlepower Lines Represented by Equation (4) or (5)*

Hence, if by means of either of the original equations (4) or (5), the loci of the point x, y for successive values of T such as met with in practice (T_0 being kept constant) be plotted and drawn, there is obtained a system of lines such as shown in Fig. 4, all the lines being curved except the one corresponding to $T = T_0$, each line of course being one of a pair of which the locus consists. In this drawing y is considered positive when measured downward from the origin, in order to have the candlepower lines slope consistently with those of the other forms of the scale hereinbefore illustrated. The particular curves shown correspond to values of T beginning with 4 candlepower for the one nearest the origin and increasing by steps of 4 candlepower for the series, the value of T_0 being 16 candlepower.

It is evident that any section cut out from the system of lines by a rectangle parallel to the X-axes, as shown in Fig. 4, is a candlepower scale similar to those already described, but adapted to photometers having both lamps stationary at a distance D apart.

Although all the candlepower lines, with the exception of the one corresponding to $T = T_0$, are curved theoretically, it is found that within the limits of a scale such as shown in Fig. 5, and indicated in correct proportion in Fig. 4, the straight line of the system lying, as it should, at the middle of the scale, the maximum deviation from a straight line, as will be shown later, is less than the accuracy within which it is possible to plot and draw the candlepower lines at their proper positions in the scale. Hence, this form of the scale may be constructed of straight lines in precisely the same manner as those already described.

2. CONSTRUCTION OF THE SCALE

When using 16 candlepower standards, it is convenient to have the 16 candlepower line at the middle of the scale, and since the straight line of the system can be made to correspond to any value chosen for T_0, let this value be 16 candlepower. Then for a photometer bench such as used in commercial work at the bureau having $D = 250$ cm, equation (4) becomes

$$x = \frac{250\,(250 - y)\sqrt{T}}{250\sqrt{T} + (4 - \sqrt{T})y} \tag{7}$$

by means of which the scale shown in Fig. 5 was computed, the dimensions of the rectangle being 8 cm by 35 cm. The upper and lower sides of the rectangle were divided into linear candlepower scales, just as in constructing the other forms, using here values of x determined by means of the above equation, and the corresponding candlepower points in the two scales were joined by *straight* lines. For the upper linear scale y had the value 121 cm, and for the lower 129 cm, these distances having been chosen so as to throw the middle point of the 16 candlepower line at 125 cm, the point midway between the lamps.

Theoretically, the maximum departure of the 13-cp line from a straight line is 0.049 mm; of the 11-cp line, 0.08 mm; and of the portion of the 9-cp line appearing, 0.03 mm. The system of curves being symmetrical with respect to the middle cp line ($T = T_0$), the same amount of curvature is to be found at the other end of the scale. Therefore, within the limits of the lines appearing in this scale, the maximum departure from a straight line in any case is so small that it is impossible, in practice, to draw a straight line so narrow that it will not cover every point of the curve.

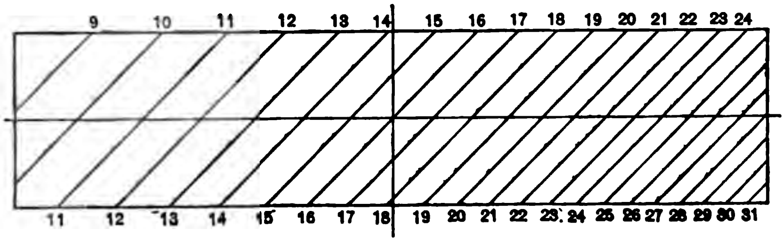


Fig. 5.—*Candlepower Scale Adapted to Photometers Having both Test and Comparison Lamps Stationary*

Since the curvature of the lines is greater the farther they lie from the line $T = T_0$, it must be determined where the curvature becomes appreciable if the scale is to be extended a considerable distance either way from $T = T_0$, and from that part of the scale to the end a sufficient number of points should be plotted for each curve to insure the required accuracy in drawing.

3. RELATIVE SENSIBILITY

Merely a glance at the two forms of the scale as illustrated in Figs. 2 and 5, respectively (which are drawn with the 16-cp line at nearly the same distance from zero; that is, at 120 cm and

125 cm, respectively), is sufficient to show that a photometer setting can be read with a greater degree of accuracy by means of the former than by means of the latter. This degree of accuracy may be called the "sensibility" of the scale and may be expressed mathematically as the derivative of x with respect to T, which, as will be seen, is a variable depending upon the value of T. Likewise the ratio of these derivatives in the two forms of the scale is a variable depending upon the value of T; but over the range of the cp lines appearing in these two forms, the average value of this ratio is approximately two, if we assume that the cp point corresponding to $T = T_0$ falls at the middle of the scale and at exactly the same distance from zero in the two cases. This may be shown in the following manner

The equation for a linear scale in Fig. 2 is

$$x = a\sqrt{\frac{T}{C_1}} \tag{8}$$

and for one in Fig. 5,

$$x = \frac{D}{1 + \sqrt{\frac{C}{T}}} \tag{9}$$

where in equation (8) a is the constant distance of the comparison lamp C_1 from the screen. Now let the cp point corresponding to $T = T_0$ fall at a distance $\frac{D}{2}$ from zero in each scale. In order that this may occur, the illumination on the comparison side of the screen must be the same in both cases when the balance is at this point; that is

$$\frac{C_1}{a^2} \text{ must equal } \frac{4C}{D^2}$$

As C and D are constants, C_1 may have any value we choose so long as a has the proper corresponding value. Let us then assume $C_1 = C$ and therefore $a = \frac{D}{2}$. Hence equation (8) becomes

$$x = \frac{D}{2}\sqrt{\frac{T}{C}}. \tag{10}$$

Now, according to the above definition, the sensibilities of the two forms of the scale as derived from equations (9) and (10) are

$$S_1 \equiv \frac{dx}{dT} = \frac{DC^{\frac{1}{2}}T^{-\frac{3}{2}}}{2(1+C^{\frac{1}{2}}T^{-\frac{1}{2}})^2}$$

and $$S_2 \equiv \frac{dx}{dT} = \frac{DC^{-\frac{1}{2}}T^{-\frac{1}{2}}}{4}, \text{ respectively,}$$

and hence their ratio is

$$R_1 \equiv \frac{S_2}{S_1} = \frac{(T^{\frac{1}{2}}+C^{\frac{1}{2}})^2}{2C}$$

which, as stated above, is a variable depending upon the value of T. At the middle of the scales where $T = T_0 = 16$, $R = 2.00$; while at the 9-cp and the 25-cp lines, $R = 1.53$ and 2.53, respectively, or an average of 2.03.

In the same manner it may be shown that the sensibility of the form of the scale adapted to photometers having both the test lamp and the screen stationary, the comparison lamp alone being movable, is

$$S_3 \equiv \frac{dx}{dT} = -\frac{DC^{\frac{1}{2}}T^{-\frac{3}{2}}}{4}$$

(derived from $x = a\sqrt{\frac{C}{T}} = \frac{D}{2}\sqrt{\frac{C}{T}}$, the equation of the scale) and that its ratio to the sensibility of the form adapted to photometers having both lamps stationary is

$$R_2 \equiv \frac{S_3}{S_1} = -\frac{(1+C^{\frac{1}{2}}T^{-\frac{1}{2}})^2}{2}$$

(the negative sign indicating that the scales run in opposite directions.)

In this case when $T = T_0 = 16$, $R = -2.00$; and at $T = 9$ cp and $T = 25$ cp, $R = -2.72$ and -1.62, or an average of -2.17.

Hence it may be stated that the form of the scale adapted to photometers having both lamps stationary is only about one-half as sensitive as either of the other two forms described.

It must not be concluded from this statement that the photometer itself is less sensitive in one case than in the others; for with the proper means of moving the photometer head back and forth by very small amounts and setting it at exactly the point desired, it should be possible, theoretically, to make settings with the same percentage accuracy, regardless of the arrangement of the photometer. The above conclusion means simply that with a setting once made the accuracy with which its position on the scale can be read depends upon the arrangement of the photometer; and hence for the most accurate work the best results are to be obtained by using a photometer having one lamp stationary with respect to the screen.

VII. SPECIAL USES OF ALL FORMS OF THE SCALE

1. READING OF RECORD PRINTED ON BLANK PAPER

Should the means of taking exact copies be not at hand it would of course, be very laborious to draw a separate scale for each set of measurements. It is a simple matter, however, by means of but one copy of the required form of the scale (whether it be continuous or sectional) carefully drawn on a separate sheet of paper or other material to read off directly in candlepower the values recorded by dots on a sheet of paper that is otherwise perfectly blank, with the exception of an index line, which may be drawn either before the paper is placed on the cylinder or at any time before it is removed by means of a pencil held at the proper point while the cylinder is given one complete turn on its axis.

The values may be read off by several different methods. By one method the record sheet and the scale sheet are clamped side by side on a drawing board, as shown in Fig. 6, with the index line of the one in line with that of the other, and readings are taken by means of a double T square provided with a fine wire stretched parallel to its edge and also with a triple right-angle sliding index (such as shown in the figure and described above) whose three straight edges are perpendicular to the wire and therefore to the edge of the T square. With the wire kept parallel to the index line and placed successively over the center of each group of record dots relative candlepower values of the standards are read from the standard scale on the 16-cp section. The wire is then set at

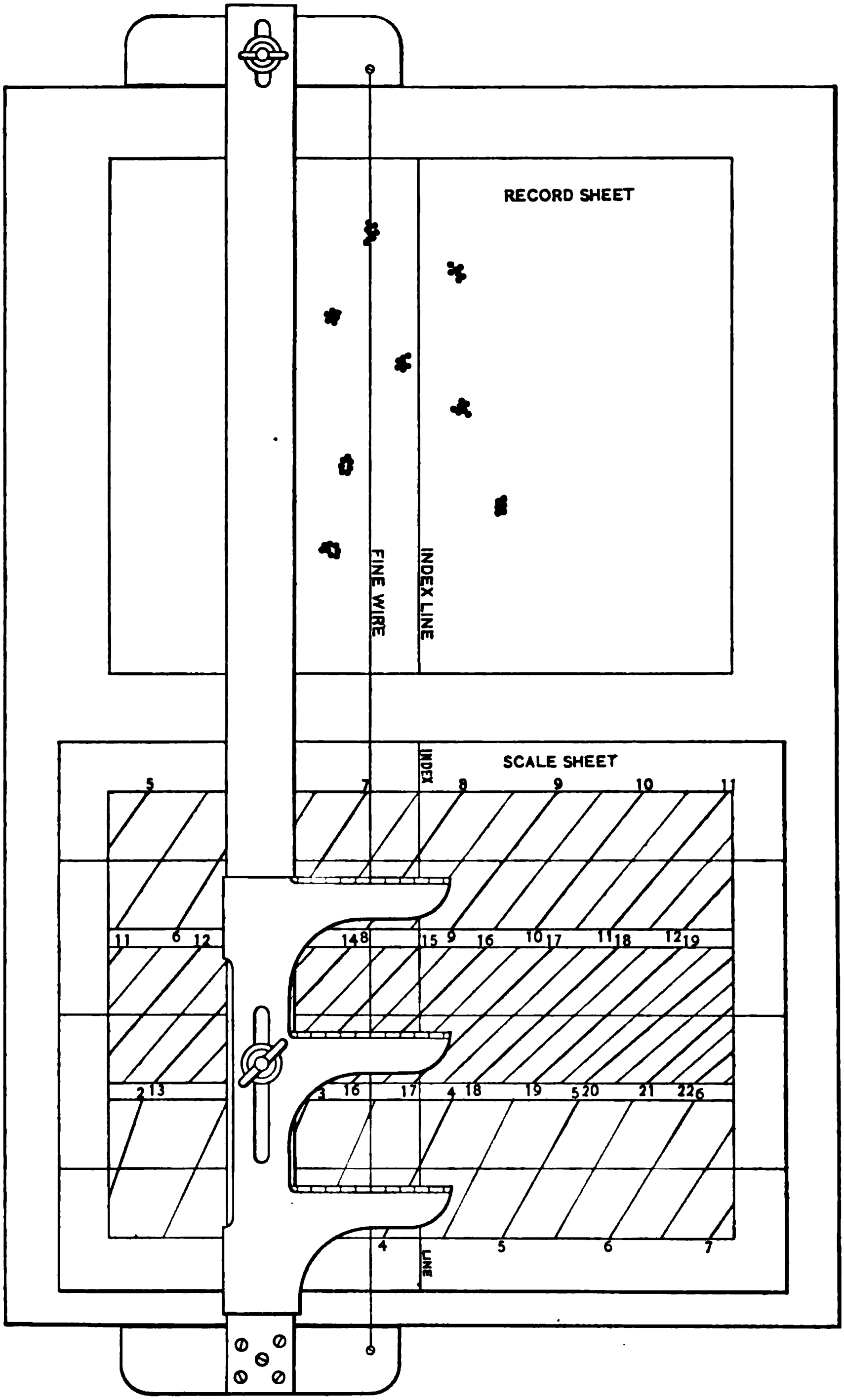


Fig. 6.—*Showing Method of Reading, by Means of the Scale, a Record Printed on a Separate Sheet.*

the mean of these readings and the triple index is moved until the intersection of its middle edge with the wire falls immediately over the exact value of the mean of the standards, at which point it is permanently clamped to the T square. Each edge of the sliding index now corresponds to a linear record scale, and the values of the test lamps may be read from the proper scale and section as fast as it is possible to set the wire over the center of gravity of each successive group of dots. The accuracy of the adjustment of the sliding index is indicated by the accuracy with which the mean of the standards, as read, equals the true value, the index being reset before the test lamps are read in case a correction is necessary. Vertical one-tenth candlepower lines may be drawn on the record sheet, if desired, by means of the edge of the T square, and the readings are then taken from the record sheet itself.

Another method of using the diagonal scale in determining the values from the record printed on blank paper is to have the scale ruled on glass or other transparent substance that will, under ordinary conditions, remain constant in dimensions. With this placed on the record sheet with the index lines superposed the values may be read off by means of the T square and sliding index in the manner described above.

Still another method is to have the record dots printed on transparent paper which may be placed over the scale with the index lines superposed, and the values may be read off directly by means of the T square and sliding index, or all the vertical one-tenth candle lines may be drawn as in the first method and the readings taken from the record sheet. The same thing may be accomplished with ordinary paper, provided the record sheet is placed over the scale sheet on a ground-glass plate illuminated from below while readings are taken or the lines are drawn on the paper. It is an advantage, whenever possible, to actually draw on the record sheet the lines mentioned, because the record is more complete and it is more easily checked by a second reader.

2. CANDLEPOWER READ DIRECTLY WITHOUT A PRINTED RECORD

Although for the sake of obtaining a permanent record, the settings are usually recorded by dots on the sheet, yet it is not at all necessary to do so. By means of a cross-hair reading index suspended from the photometer carriage the relative values of the standards may be read directly from the standard scale of the proper section which is brought immediately under the cross hair by turning the cylinder. The cross hair is then set at the mean reading of all the standards and the cylinder is turned until the reading on the scale corresponding exactly to the true value of the mean of the standards falls immediately under the cross hair. The cylinder is then clamped to prevent it from turning on its axis, and as the clock is not required, the clutch connecting it with the cylinder is released. Now as the photometer carriage is moved back and forth, the path of the intersection of the cross-hair index corresponds to the record scale on the standard section. In order to make it possible to take readings from the other two sections of the scale also, if desired, the cylinder is clamped, not directly to the frame on which it rests, but to a circular disk mounted concentrically on the same axis with itself, at the end opposite the clock, and the disk in turn is held rigid with the frame by means of a stationary pawl which engages one of three notches in its circumference, each notch corresponding to the record scale on one of the sections. This notched disk and pawl now take the part of the triple sliding index used in drawing the record scale in each section as described above. If, for instance, the standards are read from the middle section of the scale, the pawl is made to engage the middle notch when the cylinder is set and clamped to the disk and either of the other two sections is in correct position to take readings when the cylinder has been turned the proper direction and the pawl has engaged the notch corresponding to the section desired.

With the scale used in this manner, it becomes a valuable adjunct to a commercial photometer, for which purpose it may be engraved directly on the metal cylinder itself. It has all the advantages of the ordinary commercial scale and has the further advantage of quick and accurate adjustment without a tedious adjustment of the comparison lamp, which is arbitrarily set at the beginning of a set of measurements and need not be changed thereafter either in voltage or in distance.

VIII. SPECIAL METHODS OF RECORDING SETTINGS

1. WHEN RECORDING LONG OR SHORT SERIES OF MEASUREMENTS

Although a single record sheet is usually sufficient for a series of measurements on a set of lamps, yet the record may be continued on a second sheet, if necessary, without repeating the standards used at the beginning, for it is a simple matter to put the second sheet at exactly the same place on the cylinder and to draw the record scale in the same relative position on the diagonal scales on the two sheets.

On the other hand, two or more short series of measurements, made by as many different observers, may be recorded, one after another, on the same sheet. Indeed, all the different observers may make measurements on the same lamp, one after another, before proceeding to the next lamp in the set, and the different observers' values may be read off separately and correctly. Of course the position of the linear record scale may be, and most probably will be, different for each observer's record, even though no change be made in the adjustment of the apparatus, this being due to the personal equation and to a difference in the eyes of the observers. This method of measuring and recording is sometimes useful in comparing a single very special lamp with the standards.

2. WHEN STANDARDIZING AT A SPECIFIED CANDLEPOWER

In much of the bureau's work it is necessary to standardize lamps at a specified value, as for instance, 16 cp. This scale has proved itself valuable in such cases in the way of saving time, because it can be very accurately determined in advance where the reading for the required value should fall. It is customary to read three of the six standards at the beginning of a set of measurements and include the other three at the end, in order to detect any possible, accidental changes in the adjustment of the apparatus and also in order that any continuous change in the comparison lamp, or in the eye of the observer, may be eliminated in the mean of the standards and in that of the test lamps. After the first three standards are recorded their relative values are read from the standard scale and the mean determined. In making these readings the printing point is set over the center of the group to be read, the scale being brought under the point by turning the cylinder. If the value required for the test lamp is of the same nominal candlepower as the standards, then the exact difference in candlepower between the value required and the true mean value of the three standards is applied algebraically to the mean reading and the resultant value is marked at the proper point on the standard scale of the 16-cp section. For example, if the mean reading of the three standards is 16.19 cp on the standard scale, while the true value is 16.07 cp, and the value required for the test lamp is 16.00 cp, then the reading on the standard scale corresponding to this required value is 0.07 of a candle less than 16.19 cp, or 16.12 cp.

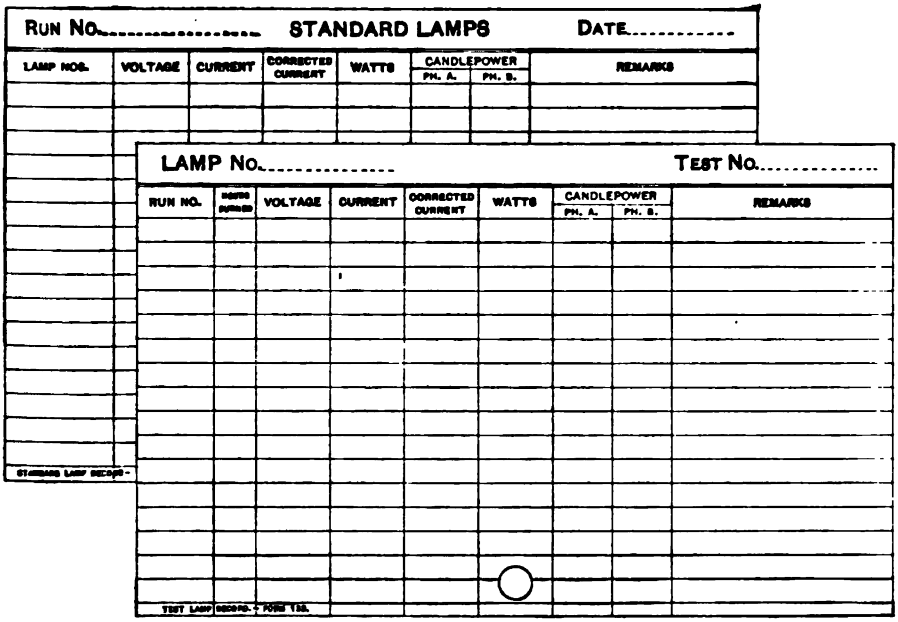
A reference line can be very readily drawn through the mark just made at 16.12 cp on the scale by the method described above, i. e., by holding the point of a pencil on the mark while the cylinder is given one complete turn. This line will, of course, be drawn upon the basis of the readings on but three of the standards and may need a small correction when the readings on the other three standards are considered, but for practical purposes it is sufficiently near to the position where the record dots for 16.00 cp should fall. This same line serves for the standardization of a lamp to be any multiple of 16.00 cp, if the proper sectored disk is used on the test side during the measurement, or any fraction of 16.00 cp if the lamp is placed at the proper point on the photometer bar, in which case the reading will, of course, be taken from the corresponding section of the scale.

The cylinder is then turned back to where the record was interrupted after the three standards were recorded, and with the printing point placed over the reference line just determined and the test lamp in the socket the voltage on the lamp is raised by the assistant at the potentiometer until the observer at the photometer is satisfied that there is a photometric balance. The voltage is then held constant while the observer proceeds to make settings and corresponding record dots. Although it is almost impossible to make the mean of the group of dots fall exactly on the reference line, yet with a little practice the observer is, in this way, able to determine very closely the proper voltage for a given candlepower value. The relation between candlepower and voltage is so well known for short ranges that any small correction that it may be necessary to apply to the observed value, to give the required candlepower, can be very accurately made by a corresponding calculated change in the voltage.

IX. MEASUREMENT AND RECORD OF ELECTRICAL QUANTITIES

1. THE ELECTRICAL MEASUREMENTS

In all the precision photometric work of the bureau the current is supplied by a storage battery carrying no other load, and both current and voltage are measured by means of a potentiometer. While the photometer settings are made the assistant at the potentiometer controls the voltage on the lamps on the two sides of the photometer and measures the current in the lamp under observation.



RUN NO.................. STANDARD LAMPS DATE............

LAMP NOS.	VOLTAGE	CURRENT	CORRECTED CURRENT	WATTS	CANDLEPOWER		REMARKS
					PH. A.	PH. B.	

STANDARD LAMP RECORD -

LAMP NO............... TEST NO...............

RUN NO.	HOURS BURNED	VOLTAGE	CURRENT	CORRECTED CURRENT	WATTS	CANDLEPOWER		REMARKS
						PH. A.	PH. B.	

TEST LAMP RECORD - FORM [illegible]

Fig. 7.—*Cards for Recording Voltage and Current and for Complete Summary*

2. RECORD OF ELECTRICAL MEASUREMENTS AND FINAL SUMMARY

In addition to making the electrical measurements, the assistant records on a filing card the current in each lamp as it is photometered, there being a separate card for each lamp (see Fig. 7) except that the record of the six standards is kept together on a single card for the sake of convenience in determining their mean and also of keeping a more condensed record of the standards. The numbers of the lamps and their corresponding voltages are entered on the cards previous to making the run, and all the test-lamp cards are linked together in the order in which the lamps are to be photometered, so that after the record dots are printed no error will be introduced in recording the numbers of the lamps in the proper order opposite the groups of dots corresponding to them. These numbers might be written on the sheet before the lamps are photometered, thus providing the observer with a check on the assistant who reads the numbers of the lamps as he places them in the socket, but it is not always possible to make the record dots fall opposite the numbers desired.

The test lamp card contains a column for the number of hours the lamp has been burned, if it required seasoning, and both the standard and the test lamp cards contain a column for corrected current and two columns for candlepower. The column for corrected current is required because when the voltage is measured by means of a potentiometer part of the current passes through the accompanying volt box, and hence a correction must be applied to the current as measured. Two columns are required for candlepower because measurements are now made by two observers at the same time on the same lamp, this being done by means of a double photometer[2] consisting of two standard photometers (referred to as photometer A and photometer B, respectively), such as already described in this paper, placed end to end, the test lamp being located at the middle where the two photometers meet. This arrangement permits double the number of measurements in a given time, requires the standards to be burned only one-half as long for a given number of measurements, and especially makes the settings of the one observer a valuable check upon those of the other.

By the data given on the candlepower record sheet (Fig. 3) and on the filing cards (Fig. 7) there is formed a complete historical record of all the work done on a lamp while under observation, and it is in such simple form as to be very conveniently filed, a complete cross reference being provided by a serial number appearing on every record sheet and card connected with any given set of measurements.

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[2] Described in the paper referred to in the introduction.

X. CONCLUSION

This combination candlepower scale and recording device has been in use in the Bureau of Standards almost daily during the past year and has proved itself entirely satisfactory. It has eliminated the computations which formerly occupied the entire time of at least one computer, and sometimes that of two. The results of a half day's work by two observers on the double photometer can be read from the scale and written on the record sheets in a few minutes, and the final record can be checked entirely by inspection. There are no tedious adjustments required and the photometer settings are recorded rapidly and accurately. The eye is not unnecessarily fatigued by alternate reading of the photometer screen and scale, and the observer is almost entirely freed from prejudice in making the settings. The record is simple, permanent, and complete, and is easily read, checked, and filed for future reference.

WASHINGTON, June 6, 1910.

A DEVICE FOR MEASURING THE TORQUE OF ELECTRICAL INSTRUMENTS

By P. G. Agnew

Different methods have been used to determine the torque of electrical instruments. A common method is to hold the instrument with the axis of the moving element in a horizontal position and place a small weight upon the needle, sliding it along the needle until the desired deflection is obtained when the needle is horizontal. The torque is then the product of the weight and its distance from the pivot.[1] It is not well adapted to such instruments as watthour meters.

A commercial instrument was developed a few years ago especially adapted to measuring the torque of watthour meters.[2] In this form the force exerted at the end of an arm attached to the moving element is transmitted to the vertical arm of a pivoted right-angled lever, the opposing force being obtained by a small weight on the horizontal arm of the lever.

Recently a somewhat similar device has been described[3] in which the force exerted by an arm attached to the moving element is measured by a calibrated coiled spring. In order to change the range, springs of different strength are substituted.

The instrument here described, while specifically designed for the determination of the torque of electrical measuring instruments, is generally applicable to the measurement of small horizontal forces.

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[1] This method seems to have been first described by Janus, Elektrotechnische Zeitschrift, **26**, p. 560; 1905.

[2] General Electric Bulletin No. 4331.

[3] Electrical World, **55**, p. 1212; May 12, 1910.

It operates on the pendulum principle, as is shown in Fig. 1, the essential feature being the use of a scale S on a concave spherical surface turned from a brass casting to a radius of curvature of 1 meter. The bob is supported from an adjustable arm and so arranged that the point of support P is at the center of curvature of the spherical scale. A silk fiber is used as suspension and is wound on a friction pin A, for convenience in adjusting its length. The fiber passes through a V-shaped notch in the end of a brass strip B, which is capable of a small horizontal adjustment to aid in the initial centering. The whole is mounted on an ordinary clamp stand, the tripod being fitted with leveling screws. The clamp C allows the scale and bob to be lowered as a unit for convenience in applying to an instrument.

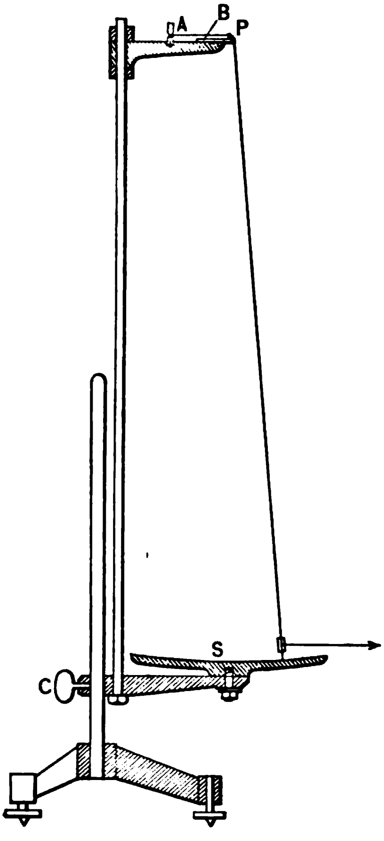

Fig. 1.—*Device for Measuring Torque.*

The graduations of the scale consist of 153 concentric circles, the distance between successive circles being approximately 1 mm. The diameter of the scale is 30 cm. Since the horizontal deflecting force varies as the tangent of the angle of displacement, it is necessary, in order that the instrument should be direct reading, that the circles should be so spaced as to read off the tangents of the angles of deflection directly. If the length of the pendulum is 1 meter and the distances between successive circles were exactly 1 mm, we would have for small angles

$$\theta = \tan\theta = .001, .002, .003, \text{ etc.}$$

To make the scale read exact tangents for the larger angles, the following method was adopted.

The hollow spherical bowl, after having been turned by the usual method, was kept in the lathe without being taken from the face plate, the screw carrying the tool post set perpendicular to the axis, and the center then carefully located by the graving tool.[4] The tool was then moved out from the center, by successive steps, the following distances measured in millimeters

$$\begin{array}{l} 1000 \sin (\tan^{-1} .001) \\ 1000 \sin (\tan^{-1} .002) \\ \vdots \\ 1000 \sin (\tan^{-1} .153) \end{array}$$

and the 153 circles engraved at these settings. A little consideration will show that this procedure makes the scale read tangents of angles directly, since the radius is 1000 mm. The scale is practically uniform.

The bob consists of a small hollow brass cylinder with a fine sewing needle passed through it perpendicular to the axis, as shown in Fig. 2. The silk fiber by which the horizontal force to be measured is transmitted to the bob is attached to the needle and passes out along the axis of the hollow cylinder. The point of attachment is made at the center of mass of the bob, which, for convenience, is marked by a file scratch. The mass of the bob alone is adjusted to 0.5 gram, but in order to change the range concentric cylinders, each cut in halves, are made to fit snugly over the inner cylinder, as is indicated in Fig. 2. These extra cylinders make the total mass 1, 2, 5, 10, and 20 grams, respectively, giving a range of 40 to 1 for full scale deflection. A radial saw-cut in each half cylinder allows these extra weights to be slipped into place without disconnecting either of the silk fibers.

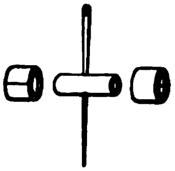

Fig. 2.—*Details of Bob.*

For the measurement of forces we have the relation

$$\text{Horizontal force} = \text{weight} \times .001 \times \text{reading in divisions.}$$

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[4] The instrument was constructed in the instrument shop of the Bureau of Standards by Mr. Rudolph Hellbach.

In measuring the torque of a deflection instrument—for example, a voltmeter—the horizontal thread is fastened to the pointer at a convenient distance from the pivot, the whole pendulum system adjusted to the proper height, and the voltmeter moved horizontally until the desired deflection is produced. We then have

$$\text{Torque} = \text{arm} \times \text{weight} \times .001 \times \text{reading in divisions.}$$

In the case of a watthour meter it is necessary only to attach the thread to the edge of the disk, apply current and voltage to the meter, and allow the thread to wind upon the disk as far as it will.

The level may be easily checked by lowering the bob until it just clears the scale and swinging it over the different parts of the scale. If it does not touch at any point, the level is correct.

Measurements may easily be made to 0.2 per cent or, if care is used in making the adjustments and the deflection kept near full scale, to 0.1 per cent.

It may be of interest to add a few numerical values to show the order of magnitude of torques ordinarily met with. The following are the least and greatest values found for three different types of instruments, several different makers being represented in each type.

D. C. voltmeters, 0.289 to 2.06 gram-cm; D. C. ammeters, 0.214 to 0.873 gram-cm; A. C. watthour meters, 3.06 to 7.74 gram-cm.

WASHINGTON, June 27, 1910.

THE INTENSITIES OF SOME HYDROGEN, ARGON, AND HELIUM LINES IN RELATION TO CURRENT AND PRESSURE

By P. G. Nutting and Orin Tugman

Lines in the spectra of luminous gases have long been known to vary in intensity with conditions in the excited gas. Some gases exhibit two quite different spectra, the primary and secondary, either of which may predominate according to the violence of the discharge causing them. Sparks between metallic electrodes give spectra richer in lines than arcs between the same metals. Additional capacity in circuit intensifies certain lines, inductance weakens them. Similar variations might be cited in great number.

To study these complex variations in spectra we have chosen three typical spectra given by gases under known conditions subject to control. Hydrogen was selected because its secondary spectrum persistently coexists with the primary even with feeble excitation and does not entirely displace it even with intense excitation. Argon gives a spectrum comparable with the spectra of many metals, intense excitation merely brings out a few additional lines. Helium is the opposite extreme from hydrogen; it persistently gives the same spectrum, no lines appearing or disappearing as the excitation is varied.

As spectral sources, we chose as the most reliable the Plücker tube operated on high potential (5000 and 10 000 volts) alternating current from transformers controlled by resistance in the low potential circuit. As the total fall of potential through our tubes was less than 1000 volts, the current wave on 5000 or 10 000 volt transformers was nearly sinusoidal. Some of the earlier work was repeated with direct current and gave the same values to 1 per cent. The first of the work was done with all-glass tubes with capillaries 2.6×60 mm and disk electrodes in spherical bulbs.

Such tubes carry a maximum current of from 20 to 50 milliamperes before showing sodium from the glass. Later we developed an end-on tube with a 3 × 30 mm porcelain capillary and large cylindrical electrodes which would safely carry half an ampere of current. The bulbs of these tubes were made of a special Corning glass which will seal to porcelain.

The method of observation was to compare the intensities of the lines from the variable tube with those from another tube kept under constant conditions. All readings are therefore relative to some fixed current or pressure. Comparisons were made with a polarization spectrophotometer. The greatest care was observed in using only pure gases and in avoiding contamination, particularly by mercury.

To avoid possible errors due to varying temperature and deterioration of the capillary wall (*V. infra*) the tubes were run on open circuit, lighting up only when a double key was pressed. Thus the tubes were spared unnecessary service and remained near room temperature. Precision milliammeters were continually in circuit with the tubes except when the disruptive discharge was used. Both ocular and collimator slits were opened to admit about 6 $\mu\mu$ of the spectrum.

HYDROGEN

Observations were made at six different regions of the hydrogen spectrum, three in the primary and three in the secondary. The readings in the secondary were made on the prominent red, green, and blue lines, α 656, β 486, and γ 434 $\mu\mu$, referred to collectively as *S*. In the primary spectrum no attempt was made to observe individual lines. A qualitative photographic test shows that the numerous fine lines vary sensibly together (except at very low pressures) and as they form, with low resolving power, a fairly uniform continuous spectrum, regions were selected for observation at about 611, 545, and 460 $\mu\mu$, referred to as *a*, *b*, and *c*, and collectively as *P*.

The data taken on the variation of spectral intensity with current are given below. The first table refers to a tube with porcelain capillary 3 mm in diameter and 30 mm long viewed end on.

TABLE I

Current in m. a.	No. obsns.	H Line-Intensity ÷ Intensity at $i=20$, $p=1$ mm			
		S_α	S_β	S_γ	P_{ave}
20	2	1.0	1.0	1.0	1.0
40	4	2.6	2.2	2.0	1.7
50	1	3.9	2.6	2.9	2.3
75	1	5.4	3.9	2.7	3.3
120	3	14.2	10.2	5.5	4.4
200	2	20.5	17.0	6.5	7.1
250	5	29.2	18.1	10.7	8.2
300	3	48.8	18.2	16.3	8.9
370	1	57.0	26.5	14.0	11.5
380	2	59.5	24.0	12.0	10.7
400	2	....	....	....	13.0
440	2	66.0	26.5	....	11.1

All values for light intensity are relative to the intensity at $i=20$. A zero reading ($i=20$) was taken just before and just after each reading at higher current and if the zero showed any shift the reading was rejected. Both tubes were filled with fresh gas at 1 mm pressure for each set of observations. The primary spectrum showed no selective (wave length) effect at even the highest currents, so the mean of the three readings is given in the last column.

These data are represented in Fig. 1. The red line is seen to vary much more rapidly with current than the others. A least square reduction for the intensity P of the primary spectrum gave

$$\frac{P}{P_{20}} = 1.042\,\frac{i}{20} - 0.0432\left(\frac{i}{20}\right)^2 + 0.00098\left(\frac{i}{20}\right)^3$$

Calling the intensity of any line L we computed values of K in $\log (L/L_0) = K \log (i/20)$. The values K were very nearly constant for each of the lines over the wide range of current used, but showed a slight and systematic lowering for intermediate currents (*150–200 m. a.*). Since the total power absorbed by the gas is the product of potential gradient (X) and current, we should expect line intensities to be simpler functions of power Xi than of current i. The gradient was determined and values are given below. Different lines should, however, be the same functions of gradient

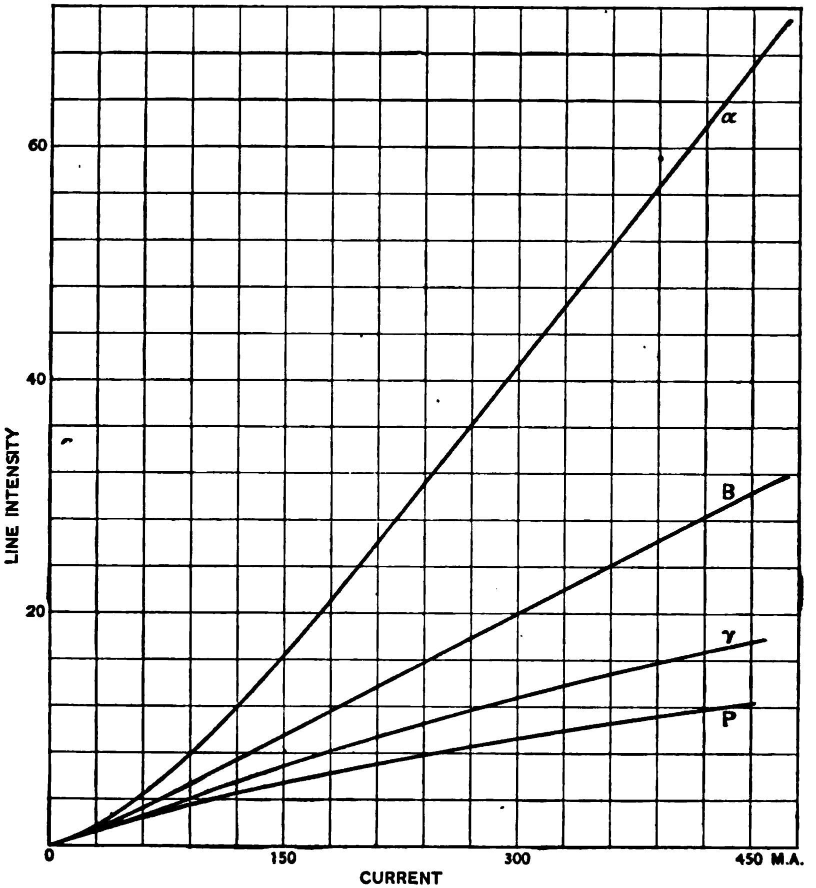

Fig. 1

and current. Taking the primary spectrum as a standard, we computed m in

$$\log \frac{\alpha}{\alpha_{20}} = m \log \frac{P}{P_{20}}$$

and similarly for the lines β and γ and obtained values of m showing *no* systematic variation with intensity. This is significant, considering the wide range of intensities covered.

We find

$$m_\alpha = 1.67,\ m_\beta = 1.35,\ m_\gamma = 1.14 \pm .02$$

Hence

$$\left(\frac{\alpha}{\alpha_{20}}\right)^{.599} = \left(\frac{\beta}{\beta_{20}}\right)^{.729} = \left(\frac{\gamma}{\gamma_{20}}\right)^{.870} = \frac{P}{P_{20}}$$

The computed uncertainty in m is about 2 per cent. It may be expressed as a function of wave length λ in

$$m = 681\left(\frac{1}{251} - \frac{1}{\lambda}\right)$$

$$m - 1 = 681\left(\frac{1}{397} - \frac{1}{\lambda}\right)$$

$$(m-1)_{\alpha,\beta,\gamma} = \frac{2}{3}(1,\ 1/2,\ 1/4 ---)$$

In Fig. 2 are plotted these values of m together with the relative energy intensities of the observed lines.

The curve for m (λ) indicates that the fourth secondary line (δ, $\lambda = 410$) would vary at the same rate ($m = 1$) as the primary spectrum, while lines farther out toward the head of the Balmer series would increase less rapidly than the primary with increase of current and hence could not be brought out prominently at this gas density with any current.

The most probable values of the spectral intensity taken from the adjusted curves are given in Table 2.

TABLE II

i	P	α	β	γ
20	1.00	1.00	1.00	1.00
50	2.1	3.45	2.72	2.33
100	3.8	9.3	6.1	4.6
150	5.4	16.7	9.7	6.8
200	6.8	24.5	13.3	8.9
250	8.2	33.5	17.1	11.0
300	9.4	42.0	20.5	12.9
350	10.4	49.8	23.5	14.4
400	11.5	59.1	27.0	16.2
450	12.3	66.1	29.5	17.4

The relative energies of the given lines given in Table 3 and plotted in Fig. 2 were obtained by comparison with a carbon filament glow-lamp whose energy-curve at a given voltage had been determined by Dr. Coblentz.

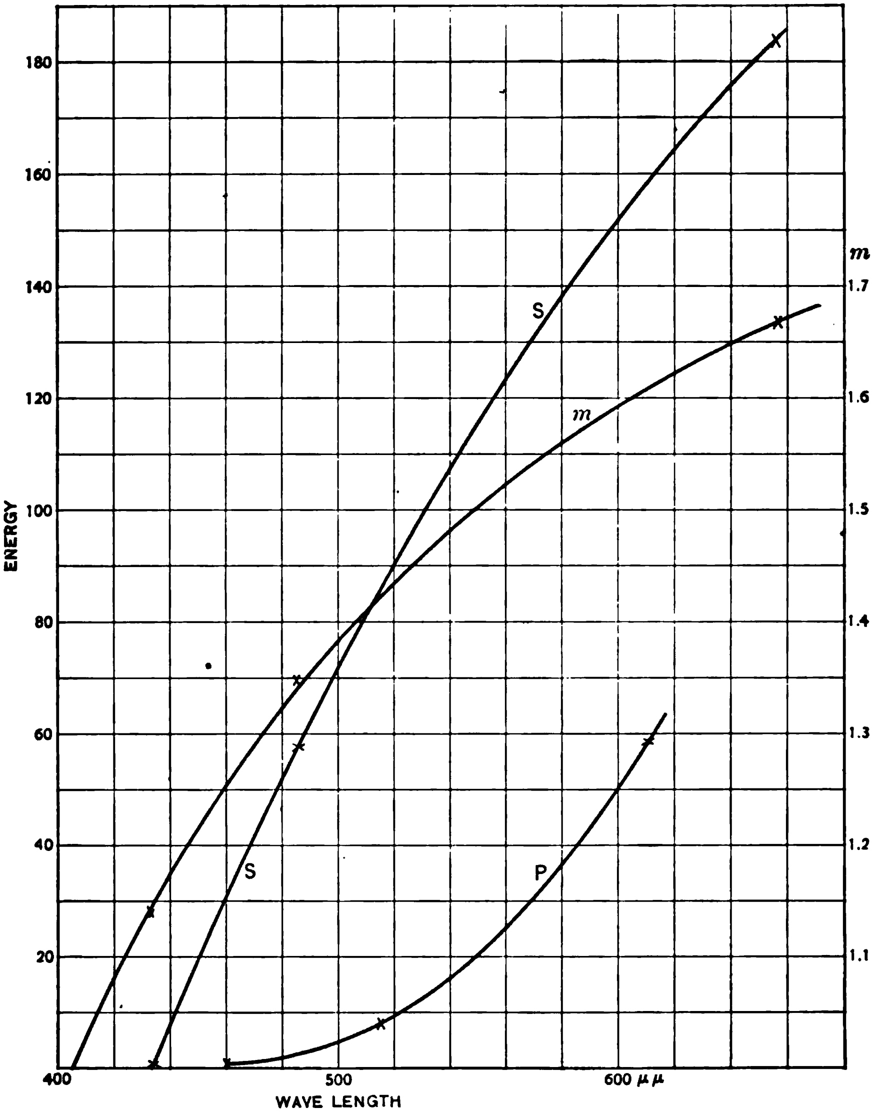

Fig. 2

The uncertainty in the data given is perhaps 5 per cent.

TABLE III

Line	λ	Lamp E	Hyd. E
α	656	197	184 ($E_{\gamma}=1$)
β	486	24	58 ($E_{\gamma}=1$)
γ	434	7.0	1
a	611	130	59.7 ($E_c=1$)
b	515	38	8.3 ($E_c=1$)
c	460	14	1.0

Considerable preliminary work was done with tubes having glass capillary portions of 2.6 mm bore viewed transversely. Data thus obtained are a useful supplement to that (above) obtained with porcelain capillary and heavy currents. In Table 4 are combined data taken with six different new tubes all of the same dimensions and each filled with fresh gas at 1 mm pressure. As neither primary nor secondary spectrum showed any selective effect, the results for each spectrum are combined.

TABLE IV

Current	2	3	5	7	9	12	15
Primary	0.16	0.24	0.34	0.49	0.65	0.81	1.0
Secondary	.04	.09	.17	.29	.42	.65	1.0

Writing as before $S/S_{15} = (P/P_{15})^m$, $m = 1.73 \pm .02$, independent of current as with large currents.

This lack of selective effect was at first attributed to lack of saturation in the thin column viewed from the side, but careful determinations at 10 m. a. made with the end-on porcelain capillary showed that there was no selective effect as large as one-third that indicated by extrapolation from higher currents.

The smallest currents at which observations were taken were 2 m.a. Fig. 3 shows that all lines vanish at or very near zero current, not at a finite value of the current as has been frequently assumed. The cause of the whiteness of the glow at low-current densities and redness at high is readily seen from Figs. 1 and 3.

The potential gradient (volts per cm) in the tubes with glass capillary 2.6 mm diameter is given in the following table. It was determined by measuring the total drop between electrodes of a tube with a long capillary before and after cutting out about 10 cm of the capillary.

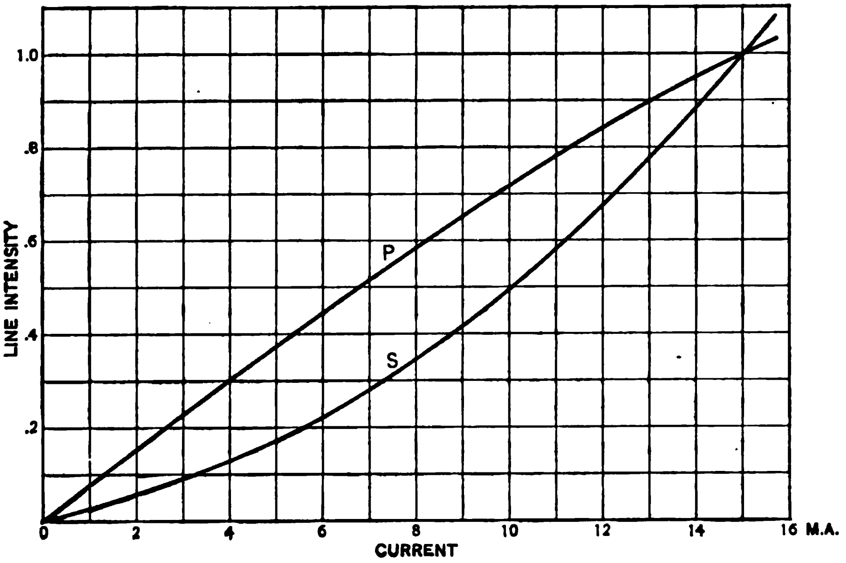

Fig. 3

Volts per cm in H, 2.6 mm Capillary

i (m.a.)	Pressure (mm)				
	0.5	1.0	2.0	3.0	8.0
2	44.5	60.2	97.0	125	191
5	37.8	56.1	90.4	107	150
9	33.7	52.1	81.1	93	128
12	34.2	50.5	74.6	84	122
15	35.8	49.5	67.4	78	120

Finally, the gradient in the porcelain capillary of the large tube was determined by measuring the drop between potential electrodes inserted at each end of the porcelain part.

Volts per cm in H, 3 mm cap., 1 mm Pressure

Current	20	50	100	150	200	250	300	350	400	450
Volts/cm	50.0	46.0	43.3	41.7	40.7	40.0	39.7	39.3	39.0	38.7

Expressing line intensity, L, as a function of internal energy $Xi = E$

$$\frac{L}{L_0} = \left(\frac{E}{E_0}\right)^n$$

Line	P	α	β	γ
$n =$	.901	1.500	1.216	1.022 ± .005

without systematic variation. The relation between m and n is $n = 0.901\ m$.

The above empirical law is consistent with a radiation function of the form

$$L = C_1\ \Lambda\ E^{\kappa} = C_1\ \Lambda e^{\kappa T}$$

in which Λ and κ are functions of wave length, and T is a function of internal energy.

GAS-DENSITY AND OTHER EFFECTS

The effect of pressure on line-intensity at constant current was studied with glass tubes similar to those last described. From several hundred observations the following mean values were adopted. No selective effect was apparent in either primary or secondary, but these differ considerably from each other. All values are in terms of those at 1 mm pressure as unity.

Pressure	Secondary	Primary
0.25 mm	0.55	....
0.50	.78	0.80
0.75	.97	.97
1.00	1.00	1.00
1.5	.90	.92
2.0	.78	.85
3	.60	.72
4	.47	.61
5	.38	.53
6	.32	.48
7	.28	.44
8	.25	.41
10	.20	.38

The current was 15 m.a. (tubes in series) and the reference tube filled at 1 mm pressure in each case. These results are shown graphically in Fig. 4.

With both tubes filled with hydrogen at 0.3, 0.5, 2, and 8 mm pressure and a current of 15 m.a. through the reference tube, readings were taken with variable current (2 to 15 m.a.) through the observation tube. These sets of readings differed very little from those taken at 1 mm pressure.

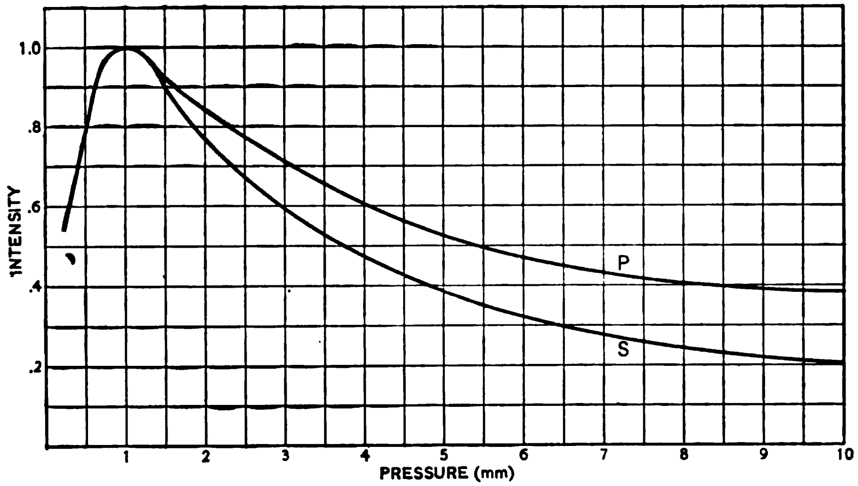

Fig. 4

Temperature of wall.—When the capillary part of a tube was heated with a flame to about 200°, α fell off 20 to 30 per cent, while β and γ and the whole of the primary were not affected by as much as 3 per cent. The tube recovers as it cools and the effect was repeated on several tubes. Since the current itself warms the tube 20° to 100°, very discordant results may be obtained unless the tubes are maintained at constant temperatures.

Effect of use.—A tube of hydrogen after half an hour of continuous operation shows a marked decrease in intensity of all lines of both spectra. After an hour's run, a purple tinge may be detected in the capillary, and if this be cut out of the tube and viewed end-on, a layer of glass less than 0.2 mm thick, next to the inner wall, will be seen to be highly colored. This coloring is not affected by moderate heating, but is completely removed by heating to the softening point of the glass; the effect increases steadily with continued use. Refilling a tube with fresh gas at the same pressure produces no measureable effect on spectral intensity.

This effect on the inner wall might be due either to negative electron bombardment or to ionization by the extreme ultra-violet waves in which the hydrogen spectrum is so rich. We are inclined to the latter view. The effect is greater for hydrogen than any other gas. A helium tube has been run a hundred hours without appreciable deterioration at a current that would have produced a 10 per cent change in a hydrogen tube in half an hour.

Oxygen with hydrogen.—Both reference tube and working tube were filled with hydrogen at 2 mm pressure, then zero readings were taken, the reference tube closed off, and an additional 2 mm of oxygen admitted to the working tube. Then with tubes in series (15 m.a. through both) it was found that the oxygen had cut down α, β, and γ about 30 per cent each, and *a*, *b*, and *c* considerably more than that amount, and *a* more than *c* so that the red primary barely showed. The net effect of the oxygen then is to make the secondary spectrum much more prominent. It is easy to see why this spectrum has so often been attributed to water-vapor. This is a rich field for further study; we have touched upon it only to guard against possible error.

In the cathode glow and striations the relation of primary to secondary varies from that in the ordinary anode column. The primary is relatively brighter (50 per cent) in the brighter parts of the striations where recombination is supposed to be particularly active. In an ordinary tube with disk electrodes and plenty of room for the cathode glow, the secondary is slightly more prominent in that glow than in the capillary; but in other tubes with cylindrical electrodes set close to the walls, the cathode's glow is nearly white and strongly favors the primary.

At atmospheric pressure a zinc spark (2 mm) in hydrogen gave hydrogen spectra not very different nor in different proportion from those in the comparison tube. The increased width of the lines, however, made a more exact comparison difficult.

A tube with fine capillary (about 0.3 mm) when adjusted to the same current-density as the reference tube gave spectra so nearly like those of the reference tube that no certain differences could be detected.

End-on effect.—Using the light from the side of a 2.6 mm capillary, we compared it with an end-on tube with a capillary portion 3.2 × 32 mm. This gave for relative intensities:

	α	β	γ	a	b	c
$\frac{\text{End-on}}{\text{Side-on}}$	1	1.35	1.58	4.37	4.37	4.39

These are relative to α, since there was an indeterminate constant factor involved. This apparently great departure from saturation may be due to a difference in the electrical conditions as the current leaves a capillary. We later obtained similar readings (not quite as high) from one end of a capillary viewed from the side.

Spark, capacity, and inductance.—The disruptive discharge was studied in considerable detail with various tubes containing gas at 1, 5, and 10 mm pressure. Two identical tubes were adjusted to 15 m.a. current, but on independent circuits, and then the discharge in one of them made disruptive, the reference tube remaining at 1 mm and 15 m.a. in each case. Some typical results are given below, the three primary readings being combined, as they remained equal throughout to within the uncertainty of measurement.

	α	β	γ	P
Pressure, 1 mm—				
Spark: No Spark	**0.59**	**0.56**	**0.60**	**0.73**
Spark+C: No Spark	**.191**	**.118**	**.063**	**.095**
S+C+I: S+C	**.22**	**.13**	**.110**	**.191**
5 mm—				
Spark: No Spark	**1.0**	**.80**	**.74**	**.90**
S+C: No Spark	**1.0**	**.35**	**.23**	**.25**
S+C+I: S+C	**.76**	**.86**	**1.22**	**1.31**
10 mm—				
Spark: No Spark	**2.30**	**1.20**	**.90**	**1.10**
S+C: No Spark	**5.88**	**2.55**	**1.00**	**.87**
S+C+I: S+C	**.50**	**.60**	**1.00**	**1.50**
Porcelain 1:1 mm 200 m.a.—				
S+C: No Spark	**.79**	**.64**	**.52**	**.46**

These results show the same selective effects as were obtained with heavy steady currents. In the first case, for example, the effect of capacity was to give α, β, and γ the ratio 3 : 2 : 1 while P lies between β and γ. These agree well with the values for a current of 200 to 250 m.a. in the porcelain tube. On the other hand, in the last case where a heavy current (200 m.a.) was used with the condenser, the effect was much less marked, about equivalent to raising the current to 300 m.a. The apparent weakening of the discharge was due to the longer interval in which no current is passing. The effect of inductance appears to be merely to neutralize part of the capacity effect. The secondary lines α, β, and γ are affected by both capacity and inductance in the order named, α most and β least.

Spectroheliographs taken with the red hydrogen line show distinctly higher levels of the solar atmosphere than those taken with the lines of shorter wave length. Our results on the effect of varying the intensity of excitation indicate just the opposite effect, the lower layers being more intensely excited should show the red line relatively more prominent than the outer layers. The selective effect of varying gas density we found to be very small over a range of pressures from 0.2 mm to 1 atmosphere, so that the observed solar effect could not plausibly be attributed to this cause. Kayser[1] holds to the view that lines of the same spectral series should vary with excitation as would portions of the same wave lengths in the spectrum of a heated cavity, a view contradicted by our results with the hydrogen secondary spectrum.

The solar effect and the end-on effect above recorded may be accounted for very simply, however, by the blanketing effect of the outer layers of a radiating gas upon the inner layers. The chief result of this blanketing being that the fainter lines in the spectrum of the inner layers would be relatively brighter than in that from the outer layers.

ARGON

The change in the argon spectrum from the "red" to the "blue" as the discharge is made disruptive is well known. The change is due to the production of additional lines in the blue and violet.

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[1] Zeit. Wiss. Phot. März, 1910.

Thus the argon spectrum behaves like the spectra of most metals and is intermediate in behavior between spectra which do not vary at all and those which vary easily and completely. These additional lines of the secondary (blue) spectrum we were able to produce in the porcelain tube without the aid of series spark or capacity and their behavior was studied at currents ranging from 450 m. a. down to about 100 m. a.

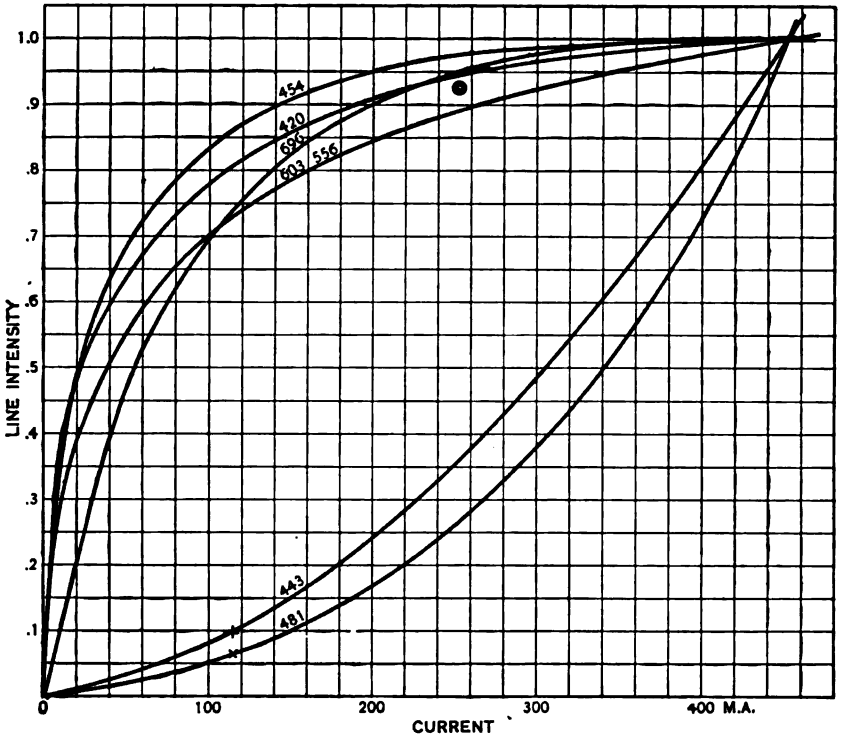

Fig. 5

We selected for study five of the most prominent lines of the primary (red) spectrum. The primary lines were: Red λ696, orange λ603, green λ556, blue λ454, and violet λ420 μμ. The secondary groups studied were at λ443 and λ481 uμ. These are in regions quite free from primary lines.

The data for argon are given in the following table and figure. The values given are graphical means of from two to six determinations at eight values of the current for the primary lines and five (115 to 450 m. a.) for the secondary, using porcelain capillary 3 mm in diameter.

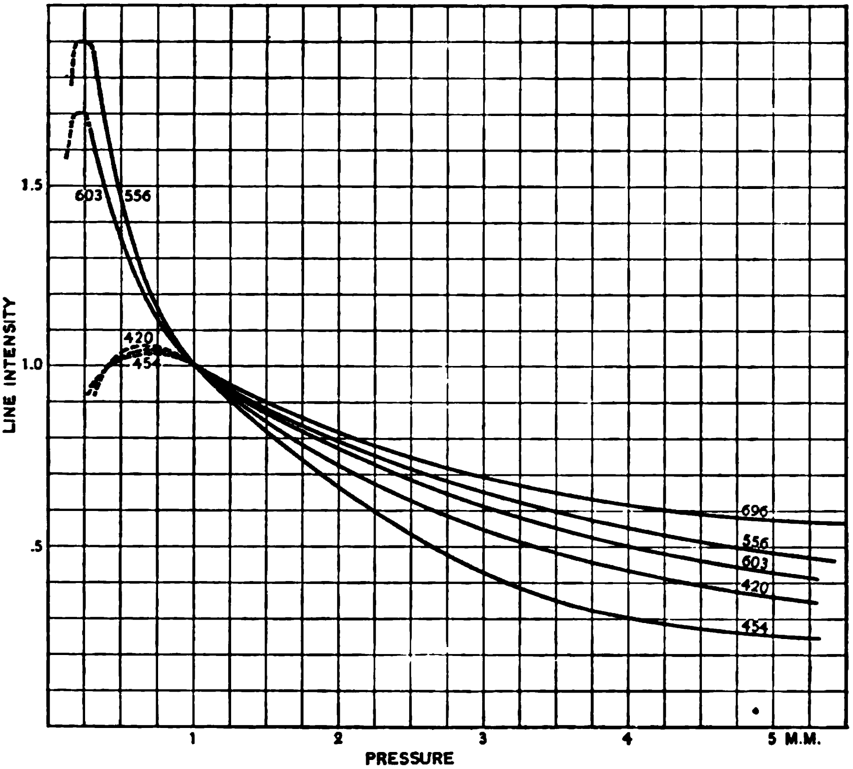

Fig. 6

Data on Argon

Current	Primary spectrum					Secondary	
	696	603	556	454	420	481	443
20	0.20	0.39	0.40	0.49	0.47	....	....
50	.47	.54	.55	.68	.62	....	....
100	.69	.70	.68	.83	.77	0.050	0.082
200	.90	.85	.83	.95	.91	.16	.24
300	.98	.92	.92	.98	.97	.37	.49
375	....	....	....	....	....	.62	.74
450	1.00	1.00	1.00	1.00	1.00	1.00	1.00

The wide departures of line intensities from proportionality with current are well shown in Fig. 5. All the primary lines rise very abruptly and then become nearly constant at high currents, while the secondary groups rise very slowly at first and then very steeply. There is no indication that these secondary lines appear abruptly at a large value of the current, but rather that they start at or near zero of current. Empirical exponential relations between the intensities of the argon lines may be set up as for the hydrogen lines, but the uncertainty in the data is so great that such relations are of little value. No determinations of the potential gradient in argon were made.

With 20 m.a. current, when condenser with series spark was added, relative intensities of primary and secondary were such as were obtained at 250 m.a. without capacity. With 200 m.a. initial current, the effect of condenser was roughly equivalent to increasing the current to 350 m.a.

In studying the effect of gas density on line intensity no attempt was made to adjust the pressure to any given value on account of the risk of introducing impurities. Sets of readings were taken first at high pressure, then after removal of a portion of the gas, and so on down to a cathode ray vacuum. This process was repeated six times and mean curves drawn through points located at the many different pressures. At pressures below 1 mm determinations differed so widely that the data in this region can be regarded as having but little more than qualitative value. Observations were made on glass tubes with 2.6 mm capillary viewed side on at the middle. The current was 20 m.a. throughout.

Argon, Line Intensity and Pressure

Pressure (mm)	Line				
	696	603	556	454	420
0.35	0.96	1.58	1.85	0.97	0.95
.70	1.04	1.16	1.21	1.03	1.06
1.00	1.00	1.00	1.00	1.00	1.00
2.00	.82	.79	.79	.67	.72
3.00	.70	.66	.66	.43	.55
4.00	.62	.55	.55	.31	.43
5.00	.58	.49	.49	.37	.25

The blue and violet lines are most sensitive to pressure changes, the red line least.

HELIUM

The helium spectrum is of the type that does not vary as the discharge is made disruptive. The cathode glow is richer in lines than the anode or capillary glow, and with disruptive discharge at low pressures these cathode lines appear in all parts of the discharge. Excluding these, we have not been able to obtain new lines with the heaviest currents and disruptive discharges available nor with pressures up to 10 mm

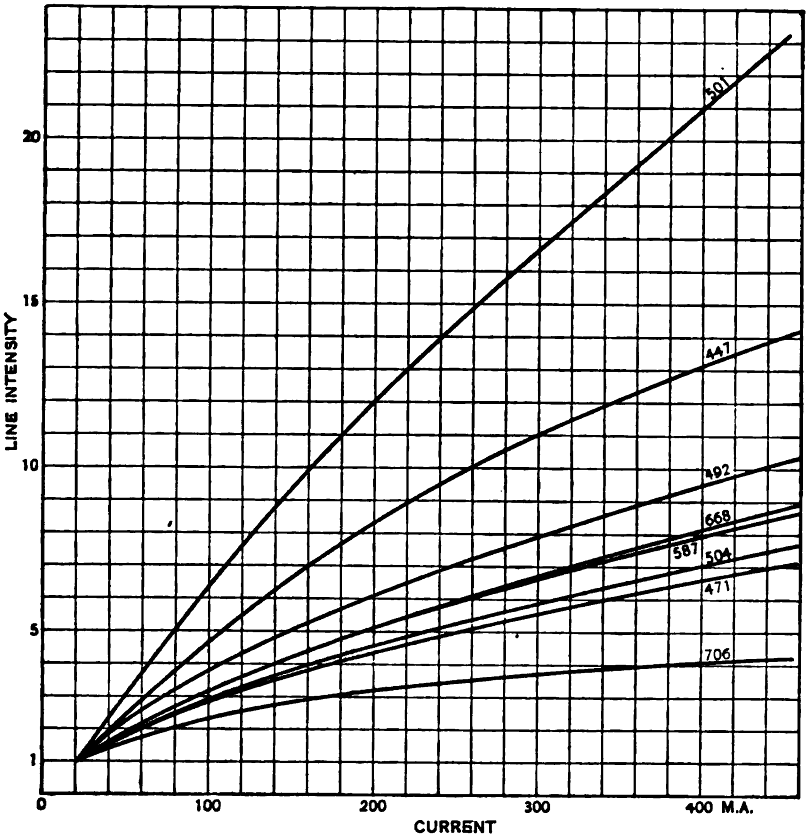

Fig. 7

The total light emission of helium per cm length of capillary as a function of current, pressure, bore, and form of current has been previously studied.[1] Preliminary results[2] on the red and blue lines 668 and 447 showed that these varied with current in sensibly the same proportion when this variation was eighteenfold, the current being varied from 2.5 to 45 m. a. in a 2.6 mm capillary. We have since extended this work to eight lines and to currents of 450 m. a. in the 3 mm porcelain capillary.

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[1] Bull. Bu. of Standards, **4**, pp. 511–523; 1908. [2] Nature, **81**, p. 189; 1909.

The lines studied were the eight brightest in the visible spectrum; the two red 706 and 667, the yellow 587, the three green 504, 501, and 492, blue 471 and 447 $\mu\mu$. The variation of line intensity with current is given in the following table. These data are graphical means of six sets of observations at seven values of the current. They were obtained with new tubes with porcelain capillary 3 mm in diameter and 30 mm long viewed end on. Another similar tube, which had previously been used for a month with argon, gave curves 10 per cent lower but of the same form.

Helium. Intensity-Current Data

Current	706	667	587	504	501	492	471	447
20	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
50	1.5	1.9	1.9	1.8	3.0	2.2	1.7	2.4
100	2.3	3.1	3.1	2.9	6.3	3.8	2.8	4.6
200	3.1	5.1	5.1	4.5	12.1	6.1	4.7	8.3
300	3.7	6.7	6.6	5.9	16.6	7.9	5.5	11.0
450	4.2	8.8	8.5	7.6	23.1	10.2	7.1	14.1

All lines increase less and less rapidly with increase in current (and energy), thus showing the characteristic of primary lines.

The potential gradient (volts/cm) in helium at various pressures and currents was determined with one of the 3-mm porcelain capillary tubes used in determining the intensity-current curves. The results are given below.

Volts per cm in He. 3 mm Capillary

Pressure (mm)	Current (m. a.)							
	5	10	20	50	100	200	300	450
1	29.8	28.8	27.4	25.3	23.4	23.3	21.6	21.0
2	30.5	29.8	28.9	26.8	24.8	23.4	22.9	22.5
4	31.3	30.7	29.8	28.0	26.5	24.8	24.2	23.7
5	32.2	31.7	30.5	28.9	27.1	25.4	24.7	24.3
6.6	33.7	32.7	31.7	29.8	28.2	26.2	25.3	24.7
10.0	35.7	35.0	34.3	32.7	30.7	28.1	27.5	27.0

The complete data on change of intensity with pressure are given in the following table. About forty observations were made on each line, using different tubes and different fillings of gas. All the data given refer to glass tubes with 2.6-mm capillary carrying 20 m.a. current (variable and reference tubes in series) viewed from the side at the middle. We also investigated the effect of pressure, using capillaries of 1-mm and of 5-mm bore, and found the variation with pressure much less in the former case and slightly enhanced in the latter (in comparison with 2.6-mm tubes).

Helium. Pressure Effect

Pressure (mm Hg)	Wave lengths of lines							
	706	667	587	504	501	492	471	447
1	....	0.8	....	2.6	1.08	1.0	1.2	0.7
1.5	0.7	.92	0.5	2.3	1.20	1.12	1.4	.9
2	.82	1.02	.8	2.0	1.28	1.20	1.4	1.05
3	1.05	1.1	1.1	1.6	1.28	1.22	1.35	1.18
4	1.02	1.1	1.1	1.25	1.15	1.12	1.15	1.15
5	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
6	.97	.95	.95	.85	.90	.87	.88	.90
7	.93	.90	.90	.72	.80	.75	.75	.79
8	.88	.85	.87	.62	.70	.68	.70	.70
9	.82	.80	.85	.55	.65	.60	.60	.65
10	.8	.77	.82	.50	.6	.52	.58	.62

The pressures at which the maximum emission occurs are higher for helium than for either hydrogen or argon.

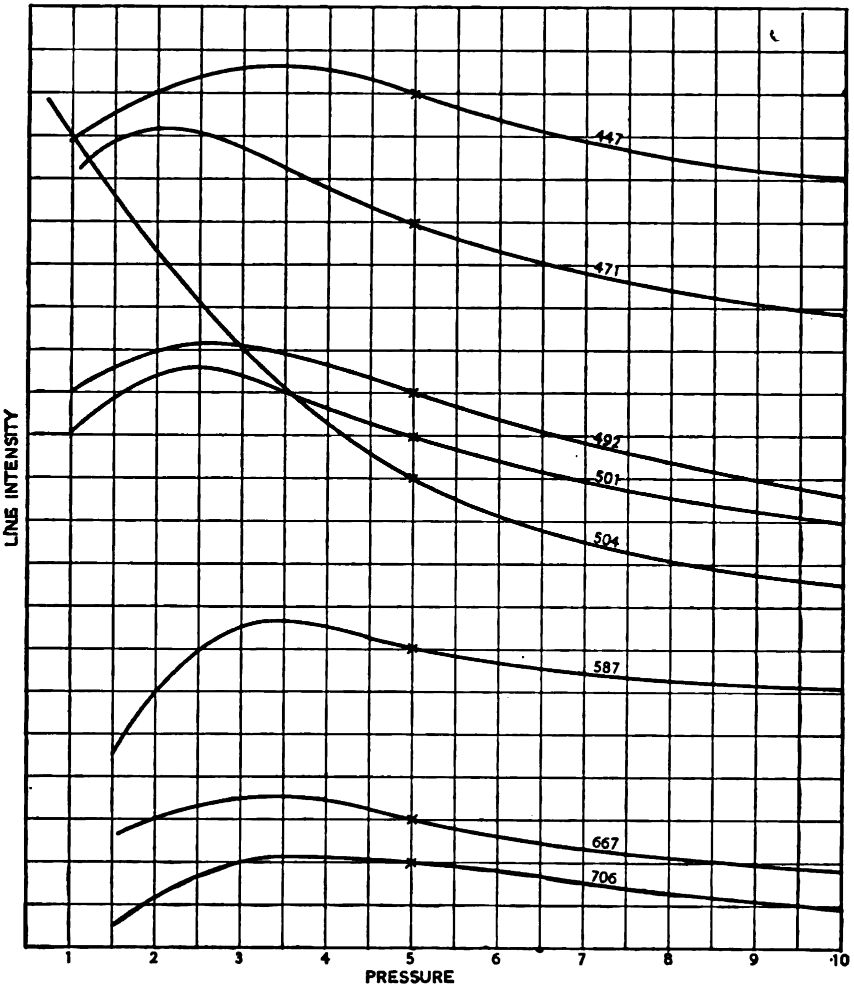

Fig. 8

DISCUSSION AND SUMMARY

This work has been done with photometer and alternating current rather than with bolometer and direct current, not only on account of the greater ease and simplicity of manipulation but on account of the much greater range of intensity that may be studied. The lower half of our curves of variation with current could hardly be obtained with bolometer or Rubens thermopile, and it is just this region that is of greatest importance. Again, in working with great current densities narrow capillaries are to be avoided on account of increased wall losses. We have used large capillaries (2.6 and 3.0 mm) throughout, and yet we regard wall losses as the chief source of uncertainty in our results.

An essential source of ambiguity in all work of this nature lies in the uncertainty in the degree of saturation (radiation compared with the radiation from a very thick layer of the same gas in the same condition) of the radiation in each spectrum line. This varies not only with each form and size of tube and each current and pressure used, but with each line or part of a line studied. In this preliminary work we have striven merely for constant, reproducible conditions, and to map out the general course of phenomena. Later work for determining radiation constants must give simultaneous measurements of radiation and absorption.

Our chief results have been the determination of line intensity as a function of current and gas density in hydrogen, argon, and helium.

All lines studied increase continuously with increase of current. The primary lines of argon and hydrogen appear to be approaching a constant intensity at the highest currents, but no lines were found which showed a decrease in intensity with increase of current.

Secondary or spark lines may be produced by merely increasing the current without the use of spark or condenser. These secondary lines do not start abruptly at a large value of the internal energy even with argon, but continue along down toward zero of current. All the lines studied fall into one or the other of two distinct classes—primary lines which increase less and less rapidly with increase in current (or internal energy), and secondary lines which increase more and more rapidly with increase in current.

The secondary spectrum of helium has no prominent lines in the visible spectrum.

The potential gradients in hydrogen and helium, in a capillary 3.0 x 30 mm, decrease rapidly at first and then more slowly with increase of current. The curves showing line intensity are sensibly the same in form when plotted with either internal energy or current as abscissas, except that the scale is slightly enlarged near the origin.

Line intensity as a function of gas density shows a pronounced maximum at from 1 to 4 mm pressure in the case of every line studied except one, He 504.

None of the lines studied contain a constant fraction of the total internal energy of the radiating gas. In other words, no line intensity is directly proportional to the internal energy. The helium lines give the nearest approach to such a law, but even in this case, with a liberal allowance for wall losses, we are convinced that no such law holds.

The intensities of some of the lines studied remain in a constant ratio independent of the internal energy. This is true, to within the uncertainty of our measurements, of the whole of the primary spectrum of hydrogen. This means that each of these lines represents a constant fraction, not of the total internal energy, but of the whole energy of the primary spectrum. Some pairs of lines (Ar 603 and 556, He 667 and 587, 504, and 471 $\mu\mu$) vary alike throughout, i. e., both lines of the pair follow the same energy law with the same parameters. As a rule, intensity curves for the different lines of the same spectrum (primary or secondary) do not cross, but the red argon line (696) is a conspicuous exception.

In one spectrum (the hydrogen secondary) the logarithmic line intensities are sensibly in a constant ratio to each other (as given in the text). In no other case have we found such a relation to hold to within the uncertainty in our results.

WASHINGTON, August 6, 1910.

THE TEMPERATURE COEFFICIENT OF RESISTANCE OF COPPER

By J. H. Dellinger

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I. INTRODUCTION

1. FORMER VALUES IN USE

Widely varying values are in use for the temperature coefficient of resistance of copper. Some of those which have been much used are given in the following table, in which α_0 and α_{20} are given respectively by the equations:

$$R_t = R_0 \ (1 + \alpha_0 \ t) \qquad R_t = R_{20} \ (1 + \alpha_{20} \ [t - 20])$$

R_0, R_{20}, R_t = resistance respectively at 0° C, at 20° C, and at t°. t = any temperature centigrade.

	α_0	α_{20}
Matthiessen's temperature coefficient, 0° C to 20° C	0.00398	0.00369
Laboratoire Central d'Électricité	.00400	.00370
Kennelly and Fessenden, 1890	.00406	.00375
American Institute of Electrical Engineers	.00420	.00387
Verband Deutscher Elektrotechniker	.00426	.00392
(British) Institution of Electrical Engineers	.00428	.00394
Lagarde, 1893	.00445	.00409

Matthiessen's formula is: $\lambda_t = \lambda_0 \ (1 - 0.0038701 \ t + 0.000009009 \ t^2)$. λ_t and λ_0 = conductivity, or reciprocal of resistance, at t° and 0° C, respectively.

The second value given is that used by French engineers. The value given by the American Institute of Electrical Engineers has also been assumed by the Bureau of Standards. The value given by the Verband Deutscher Elektrotechniker has been in general use in Germany since 1896, and was obtained by assuming $\alpha_{15} = 0.004$. The relations between α_0, α_{15}, etc., are given in Section IV of this paper. The British Institution of Electrical Engineers' value is based on the measurements of Clark, Ford, and Taylor, in 1899, and happens to be the same as that determined by Dewar and Fleming in 1893. Matthiessen's two-term formula, published in 1862, is given in terms of conductivity instead of resistance, and has been used probably more than any other. Inasmuch as a linear formula suffices to express the accuracy of all work done up to the present for moderate temperature ranges, and as the many digits of Matthiessen's coefficients are without significance (the first being the mean of a number of values ranging from 0.0037351 to 0.0039954), it is evident that the further use of this formula is undesirable.

2. NECESSITY FOR THE PRESENT INVESTIGATION

The variations of the values in the above table may be considered to be due either to errors of the measurements made in establishing them or to differences in the temperature coefficients of different samples of copper. In either case, accurate results can not be expected when one of these values is taken as fixed and used for all samples. That this fact is not recognized is shown by the common practice of assuming that the temperature coefficient is the same for different samples of copper, while the conductivity is usually measured. It was accordingly considered of importance to determine whether the temperature coefficient of different samples does vary, and also to find whether there is any simple relation between the conductivity and the temperature coefficient.

An investigation has been carried out with the above in view upon samples of copper which represent a considerable number of the chief sources of supply of the copper used for electrical purposes and which include the native metal, that refined by smelting, and that refined by electrolysis. The results show that there are variations of the temperature coefficient, and that to a fair accuracy the relation of conductivity to temperature coefficient is a simple proportionality. This relation is in corroboration of the results of Matthiessen and others for differences in conductivity caused by chemical differences in samples; but the present results show that it holds for both physical and chemical differences. Thus, hard-drawing and annealing, even more exactly than changes in chemical composition, cause proportional changes in conductivity and temperature coefficient.

II. EXPERIMENTAL DATA

The experimental work was carried out with wires, sizes 6 to 12, Brown & Sharpe gage, of about 120 cm length. The resistivity and percent conductivity were computed from measurements of the length, mass, and resistance. The resistivity is given in ohms per meter-gram by multiplying the resistance per meter by the mass per meter. The "percent conductivity" is calculated on the assumption of 100 percent conductivity corresponding to a resistivity of 0.153022 ohm per meter-gram at 20° C.[1] According to practice that is now very general in scientific work, 20° C is used as the standard temperature instead of 0° C. The final results will be given, however, for 0° C, 15° C, 20° C, and 25° C, and they can be computed for any temperature.

---

[1] This is the value assumed by the Bureau of Standards as representing "Matthiessen's standard," an arbitrary standard in wide use commercially. This value corresponds also to 1.72128 micro-ohms per centimeter cube at 20° C on an assumed density of 8.89.

1. THE RESISTANCE MEASUREMENTS

For the resistance measurements the wires were placed in a specially designed oil bath with provisions for efficient stirring of the oil, for heating and cooling, and for temperature regulation. The wire was held between heavy clamps through which the current was introduced. For conductivity determinations the resistance was measured between knife edges mounted 1 meter apart on the marble base. The Thomson bridge method was used for measuring the resistances, employing a double set of variable ratio coils; an accuracy of 1 in 10 000 was easily attained. The resistance of the copper sample was compared with the resistance of a copper standard in the same bath as the test sample. The copper standards were wires carrying soldered potential leads and placed in frames having connections for both current and potential leads. These connections dropped into mercury cups on the marble base in the oil bath. The resistances of the copper standards were compared from time to time with manganin resistance standards which were kept in a separate oil bath. The method of comparing the copper samples with a copper standard has the advantage that accurate temperature measurement is unnecessary.

2. THE TEMPERATURE COEFFICIENT MEASUREMENTS

For the measurements of the temperature coefficient, potential terminals were used. The resulting temperature coefficient is therefore that of "constant mass." (See page 92.) The terminals were soft-soldered to the wires a little over a meter apart. Measurements of the resistance between the meter knife-edges before and after soldering on the potential terminals showed differences in general well below 1 in 10 000. Hence it may safely be assumed that the soldering did not appreciably alter the conductivity. The temperature coefficient was measured by comparing the resistance of the sample at two or more temperatures with the resistance of a copper standard in the same bath. This gave the difference between the temperature coefficients of the sample and of the standard, and as the difference was always small the temperature measurements did not have to be made with great accuracy. The temperatures used in these comparisons were between 20° C and 50° C, the range being always greater than 10° C. The temperature coefficients of all the samples were measured against the same copper standard. The relative accuracy of the resulting values of the temperature coefficient is therefore high and is estimated as within ±0.000 004 (or 0.1 per cent).

The absolute accuracy of the temperature coefficient values depends on measurements which were made upon three of the samples, for a range of 12° C to 100° C. The resistances (of two of these) were compared against manganin standards at constant temperature, and the temperatures measured with a mercury thermometer at approximate 10° intervals in this range. (The third was measured only at 25° C, 55° C, and 100° C.) The measurements were made in a well-stirred oil bath. It was ascertained that no appreciable errors were introduced by conduction of heat through the leads of the wire under observation, and that the temperature was sufficiently uniform to permit of accurate temperature measurement. To the thermometer readings were applied calibration, ice point, and emergent stem corrections. The accuracy of the resistance measurements was within 0.004 per cent, and the precision of reading the thermometer was within 0.03° C. The higher temperatures were not known to this accuracy, however, because of the large correction for emergent stem. Thus at 100° C the stem correction was uncertain by 0.2° C, which makes the computed value of the temperature coefficient uncertain by 0.000 01, or 0.2 per cent. The accuracy of the computed values of the temperature coefficient from the observations below 70° C is estimated as within 0.000 004, or 0.1 per cent; the relative values of the temperature coefficients of the three wires as obtained from these measurements, and as obtained by measurement against the copper standard, agree well within this accuracy. Within the limits of accuracy stated, for the range of 12° C to 100° C, the temperature coefficient was found to be linear. The important range of temperature in commercial work extends to about 75° C. The temperature coefficient is here shown to be accurately linear up to this temperature, and if there is any departure from a linear relation between 70° C and 100° C it is inappreciable in commercial work.

The results of the measurements on the separate samples are given in the table below. In each case α_{20} is divided by the percent conductivity and the quotient given under C. C, the constant resulting, is the computed value of the temperature coefficient of copper of 100 percent conductivity.

TABLE I

Temperature Coefficients (1) Observed, and (2) Computed for Copper of 100 Percent Conductivity

Percent conductivity[2]	α_{20} $\left(=\frac{R_t-R_{20}}{R_{20}[t-20]}\right)$	C $\left(=\frac{\alpha_{20}}{\text{Percent conductivity}}\right)$	Mean values of C	Deviations from final mean
[3] 97.44	0.00384_0	0.00394_1		
[3] 97.46	384_3	394_3		
[3] 97.54	384_6	394_3		
100.22	395_0	394_1	0.00394_2	$+0_4$
100.24	395_2	394_3		
100.29	395_4	394_3		
100.44	395_9	394_2		
[3] 97.47	382_5	392_4		
100.11	393_1	392_7	$.00392_6$	-1_2
99.96	392_7	392_9		
100.09	392_9	392_6	$.00392_7$	-1_1
[3] 98.18	386_0	393_2		
[3] 98.25	386_0	392_9	$.00393_0$	-0_8
99.73	393_5	394_6		
100.16	393_6	393_0	$.00393_8$	0
[3] 96.56	380_6	394_2		
[3] 96.96	382_8	394_8		
99.63	391_7	393_2	$.00393_7$	-0_1
99.97	392_7	392_8		
[3] 94.13	371_6	394_8		
[3] 95.80	378_2	394_8		
96.60	381_5	394_9	$.00394_9$	$+1_1$
99.89	394_6	395_0		
[3] 97.07	384_0	395_5		
99.75	394_0	395_0	$.00395_2$	$+1_4$

[2] 100 percent conductivity corresponds to resistivity of 0.153022 ohm per meter-gram (or 1.72128 micro-ohms per centimeter cube, density=8.89), at 20° C.

[3] Hard-drawn wires; the others are annealed.

TABLE I—Continued

Percent conductivity[2]	α_{20} $\left(=\frac{R_t-R_{20}}{R_{20}[t-20]}\right)$	C $\left(=\frac{\alpha_{20}}{\text{Percent conductivity}}\right)$	Mean values of C	Deviations from final mean
[3] 97.96	0.00385_3	0.00393_3	0.00393_2	-0_6
100.70	395_9	393_2		
99.14	392_6	396_0	$.00395_6$	$+1_8$
99.39	392_8	395_2		
[3] 96.95	383_0	395_0	$.00394_3$	$+0_5$
100.26	394_6	393_6		
[3] 97.84	385_0	393_5	$.00393_2$	-0_6
100.54	395_1	393_0		
[3] 97.25	382_8	393_6	$.00393_4$	-0_4
100.14	393_8	393_3		
[3] 97.75	384_5	393_3	$.00393_1$	-0_7
100.70	395_7	392_9		
				Mean deviation
Final mean			$.00393_8$	$=0_8$
Final mean rounded off			.00394	=0.2%

[3] Hard-drawn wires; the others are annealed.

3. THE SOURCES OF MATERIAL REPRESENTED

Each one of the groups into which the results are divided represents one source of material. These sources, without reference to the order in the table, were the following:

Smelters	Calumet and Hecla Smelting Works, Hubbell, Mich. Quincy Mining Company, Hancock, Mich. Buffalo Smelting Works, Buffalo, N. Y.
Electrolytic refiners	American Smelting and Refining Company, Maurer, N. J. The Baltimore Copper Smelting and Rolling Company, Baltimore, Md. The United States Metals Refining Company Chrome, N. J. Raritan Copper Works, Perth Amboy, N. J. Nichols Copper Company, Laurel Hill, N. Y. A. Grammont, Pont-de-Chéruy, France.

Wire manufacturers	American Brass Company, Waterbury, Conn. John A. Roebling's Sons Company, Trenton, N. J. Standard Underground Cable Company, Perth Amboy, N. J. Heddernheimer Kupferwerk und Süddeutsche Kabelwerke, Frankfurt-am-Main, Germany. Kabelfabrik - und Drahtindustrie - Actien - Gesellschaft, Vienna, Austria.

Most of these companies kindly furnished the samples of copper wire at the request of the Bureau of Standards. This opportunity is taken of expressing appreciation for the cooperation of these companies. Some of the refiners were represented only in the samples submitted by one of the wire manufacturers. One sample was from an ordinary purchase of wire.

It will be seen that a considerable number of the most important producers of copper are included in the list. This country, Germany, France, and Austria are represented. As the samples (except three; see next paragraph) were the usual commercial grade of copper that is sold for electrical purposes, and as the range of conductivity of the samples covers thoroughly the range of such copper, it is believed that the results are representative. The third column of the table shows the agreement of the samples from each source. The fourth column shows the agreement of the various sources. The fifth column gives the deviations of the group means from the final mean. The mean deviation is 0.000 008, or 0.2 per cent. The experimental error of the separate measurements is probably not greater than 0.000 004, or 0.1 per cent. However, in view of all the circumstances, the mean deviation is remarkably small, and we are justified in saying that the accuracy of the final mean is probably well within 0.000 01.

4. EFFECT OF CHEMICAL DIFFERENCES OF SAMPLES

The agreement of C for samples differing in chemical composition is shown throughout the list, and in particular by the seventh group. The samples in this group were of copper refined by smelting. The first three samples of this group are the only ones given in the list which do not represent the usual copper which is sold and accepted for use as electrical conductors. The first is a hard-drawn wire and the third an annealed wire of "cupola" copper, known to be highly arsenical. The second is a hard-drawn wire of "silver-bearing" copper, containing 0.17 per cent silver. The fourth in the group is the regular refined copper of the smelter. Chemical analyses of the refined copper and the cupola copper, which were furnished by the smelting company, are given herewith:

	Refined	Cupola
Copper	99.88	99.85
Silver	0.0710	0.0570
Arsenic	.0006	.0099
Lead	None	Trace
Iron	.0014	.0063
Sulphur	.0022	.0064
Zinc	Trace	.0008
Nickel	.0010	.0108
Antimony and gold	Faint trace	Faint trace
Bismuth, selenium, and tellurium	None	None
Oxygen, by difference	.0450	.0560

The arsenic alone is sufficient to account for the low conductivity of the cupola copper.

5. EFFECT OF PHYSICAL DIFFERENCES OF SAMPLES

The agreement of C for samples differing in physical condition is shown by the first, second, sixth, eighth, ninth, eleventh, twelfth, thirteenth, and fourteenth groups. The wires indicated by a superior figure (^{3}) were hard-drawn; the others were annealed. *The effect of hard-drawing and annealing was further tested.* A piece of the same soft wire from which was taken the fifth sample in the table was partially hardened by drawing through dies, and the measurements showed

$$\text{conductivity} = 98.96\%, \ \alpha_{20} = 0.003902, \ C = 0.003943$$

Also, a piece of the hard-drawn wire given second in the table was annealed by heating electrically to a dull-red heat and gave the following

$$\text{conductivity} = 100.15\%, \ \alpha_{20} = 0.003948, \ C = 0.003942$$

Again, the identical sample given first in the table was annealed, and gave

$$\text{conductivity} = 100.14\%, \ \alpha_{20} = 0.003946, \ C = 0.003941$$

The agreement of C before and after the alteration of physical condition in all cases is within the experimental error.

6. EFFECT OF LOCAL HARDENING

The effect of local hardening of a wire was also investigated. This is of importance because in ordinary use copper wire is bent and coiled. Bending is known to produce local hardening and increase of resistance. The increase of resistance is usually considered to be due simply to increase of specific resistance, just as the hardening of a wire by drawing increases the specific resistance. It would therefore be expected that the temperature coefficient would increase as does the resistance. That this view is in error was shown by the following experiments. An annealed wire was bent back and forth at a number of points, and the resistance and temperature coefficient remeasured. The apparent conductivity decreased, while the temperature coefficient scarcely changed at all. The wire was then annealed and remeasured. The results are given in the following table:

	Percent conductivity	α_{20}	C
Before bending	100.11	0.003931	0.003927
After bending	99.31	.003926	....
After annealing	99.48	.003929	....

Another annealed wire was treated more severely, bent, pulled, twisted. The results are given in the following table:

	Percent conductivity	α_{20}	C
Before distortion	100.44	0.003959	0.003942
After distortion	98.35	.003931	....
After annealing	98.90	.003953	....

In this case the apparent conductivity showed a large decrease upon distortion, and the temperature coefficient a slight decrease. We therefore conclude that most of the apparent decrease in conductivity is due to some such cause as change of cross section. This conclusion is strengthened by the result of the annealing. If the decrease in conductivity were due simply to a hardening, we should expect that the annealing would restore the former conductivity. But we see that the annealing actually raises the apparent conductivity only slightly and raises the temperature coefficient a proportionate amount, in fact restoring practically the original temperature coefficient. The greater part of the decrease in apparent conductivity, due to local distortions, is therefore, caused by local changes in cross section. Ordinary bending, as seen from the first of these two wires, changes the temperature coefficient practically not at all. It will be noticed that the value of C is not computed for the distorted wires in the two preceding tabulations. This is to emphasize the fact that a correct value of C is not obtained with samples which have been bent and distorted; as may be seen, in these cases the value of C would be too high. In the measurement of conductivity the assumption of a uniform sample must be carefully guarded, while this is not necessary in the measurement of temperature coefficient. This will be discussed below.

7. COPPER SAMPLES THAT HAD NEVER BEEN MELTED

Besides the results already given, measurements were made upon some samples of electrolytic copper wire drawn directly from cathode plates without intermediate melting. These were of especially high conductivity because of high purity, the chief gain in conductivity probably being due to freedom from the cuprous oxide introduced in melting. The results were:

Percent conductivity	α_{20}	C
101.33	0.003972	0.003920
101.35	.003969	.003916
101.50	.003976	.003917
[4] 99.46	.003896	.003917

[4] Hard-drawn.

The first two samples were from one of the electrolytic refiners mentioned above, and the third and fourth from another; the first three samples were annealed, the fourth was hard drawn. These results for C lie slightly below any of the values in the table above.

They were omitted from the table because this cathode copper was specially prepared for experimental purposes, and the table is intended to represent simply the copper commercially obtainable. Further, there is evidence that wires prepared from the cathode plates are not as homogeneous as the ordinary copper. Thus some of the wires had a longitudinal black line the whole length of the wire. This appeared to be the result of a creasing over of the surface layer by the hammering process which was used to prepare the plates for drawing; the surface layer probably contained iron and oxide and other impurities. The view that the low values of C are due to inhomogeneities which are not present in the ordinary copper which has been melted is strengthened by a further experiment. The samples were annealed at a dull red heat; the results then were:

Percent conductivity	α_{20}	C
101.39	0.003982	0.003927
101.54	.003983	.003922
101.53	.003984	.003924
101.41	.003980	.003925

Cathode copper is known to occlude considerable quantities of hydrogen.[5] We might, therefore, expect abnormalities in its properties. The precise explanation of the original low values for C is not, however, apparent; if there were defects in these wires in the nature of local discontinuities we should expect the apparent conductivity to be less than the real conductivity, and the temperature coefficient to be unaffected; hence the value of C would be too high.

Another anomalous case found was that of some native lake copper which had never been melted down. The wires had been drawn directly from the mass of native copper. Annealed, it had higher conductivity and temperature coefficient than any other copper as yet measured at the Bureau of Standards (except that the temperature coefficient of the above-mentioned cathode copper was higher after re-annealing). The results follow; the first is a hard-drawn wire, the second annealed.

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[5] Soret – Comptes Rendus **107**, p. 733; 1888, and **108**, p. 1298; 1889. Foerster – ZS Electrochem. **5**, p. 508; 1899.

Percent conductivity	α_{20}	C
99.17	0.003885	0.003918
101.71	.003978	.003911

It is to be noted that both these wires and the cathode samples of the preceding paragraph were prepared from copper that had not been melted.

III. CONCLUSIONS

1. PROPORTIONALITY OF TEMPERATURE COEFFICIENT AND CONDUCTIVITY

The principal result of this investigation may be expressed in the form of the following practical rule: *The 20° C temperature coefficient of a sample of copper is given by multiplying the number expressing the percent conductivity by 0.00394.* (100 percent conductivity is taken as corresponding to a resistivity of 0.153022 ohm per meter-gram at 20° C.) This is intended to apply merely to the copper furnished for electrical uses, and to the temperature range of 10° C to 100° C, over which the temperature coefficient was found to be linear. The practical importance of this relation is evident, for it gives the temperature coefficient of any sample when the conductivity is known. Thus, the temperature coefficient for the range of conductivity of commercial copper may be exhibited by the following table:

TABLE II.

Temperature Coefficients of Commercial Copper

$R_t = R_{t_1}(1+\alpha_{t_1}[t-t_1])$

Ohms per meter-gram at 20° C	Percent conductivity	α_0	α_{15}	α_{20}	α_{25}
0.15940	96%	0.00409	0.00386	0.00378	0.00371
.15776	97	.00414	.00390	.00382	.00375
.15614	98	.00418	.00394	.00386	.00379
.15457	99	.00423	.00398	.00390	.00383
.153022	100	.00428	.00402	.00394	.00386
.15151	101	.00432	.00406	.00398	.00390

The above table was calculated by means of the following formula, which holds for any temperature, t_1, and any percent conductivity, n (expressed decimally—e. g., if percent conductivity = 99 per cent, $n = 0.99$):

$$\alpha_{t_1} = \frac{1}{\frac{1}{n\,(.00394)} + (t_1 - 20)}$$

2. THE RESISTIVITY-TEMPERATURE CONSTANT

Conductivity tests are made in connection with the purchase of wire by many refiners, wire manufacturers, makers of instruments, and others. A knowledge of the temperature coefficient is important in the determination of conductivity when the measurements are made at a temperature other than the standard temperature. Our rule can be put in a remarkably convenient form for such cases, viz: *The change of the resistivity per degree C of a sample of copper is 0.000598 ohm per meter-gram, or 0.00681 micro-ohm per centimeter cube.* Accordingly the resistivity as found at any temperature may be reduced to standard temperature simply by adding one of these constants multiplied by the temperature difference. These constants are independent both of the temperature of reference and of observation, and also independent of the sample of copper.

3. TEMPERATURE CORRECTION FOR MEASUREMENTS AGAINST A COPPER STANDARD

When a determination of conductivity involves a resistance measurement against a copper standard at the same temperature as the test sample, usually no temperature correction is necessary. When, however, an accuracy of 0.01 per cent is striven for, it is often necessary to make a correction. In such cases the meter-gram resistivity at the standard temperature, T, is obtained by adding to the meter-gram resistivity as calculated from the resistance comparison at $t°$, the quantity $[(t - T)\ (\delta - \delta_n)\ (0.0039)]$; in which δ = meter-gram resistivity of the sample and δ_n = quotient of 0.000598 by the temperature coefficient of the copper standard. Similarly the centimeter cube resistivity at the standard temperature is obtained by adding to the centimeter cube resistivity as calculated from the resistance comparison at t°, the quantity $[(t-T)\ (\rho-\rho_n)\ (0.0039)]$; in which ρ = centimeter cube resistivity of the sample and ρ_n = quotient of 0.00681 by the temperature coefficient of the copper standard.

4. EFFECT OF HARDENING, IMPURITIES, AND DISTORTION ON THE TEMPERATURE COEFFICIENT

A conclusion which follows from the results is that the resistance added to that of pure copper by hardening or by the presence of the small quantities of impurities usually found in refined copper has no temperature coefficient. That is, when the resistance of a piece of copper is changed by the addition of small quantities of impurities or by hardening, the absolute change of resistance with temperature is unaffected, while the percentage change of resistance with temperature is affected. On the other hand, when the resistance is changed by an alteration of dimensions the absolute change of resistance with temperature is affected and the percentage change of resistance with temperature is not. From the latter fact may be drawn a practical conclusion concerning the local hardening and distortion of a wire. As shown above, the ordinary coiling, winding, and bending of a wire may increase its resistance. In such cases there are local changes of dimensions which are much more effective in changing the resistance than the slight hardening caused, and thus such distortions do not materially affect the percentage temperature coefficient. It may therefore be assumed without serious error that the temperature coefficient of a copper wire is the same after winding on a machine or instrument as it was before. Accordingly, if a measurement has been made of either the conductivity or the temperature coefficient of the wire before winding the temperature coefficient may safely be assumed to be known after winding and may be used in the calculation of temperature rise.

Although the agreement of the values for C indicates that it is a real constant for copper, there are still variations from the mean greater than the experimental error. The higher values of C are possibly explainable on the basis of local distortions of the samples, which would give wrong values for the conductivity, as above.

The lower values, particularly those for the cathode copper and for the native lake copper, are not explained. Perhaps all the variations are due to differences in the treatment of the metal, or to the varying effect of the different chemical impurities upon the conductivity and temperature coefficient.

5. THE TEMPERATURE COEFFICIENT AS A MEASUREMENT OF CONDUCTIVITY

The relation between conductivity and temperature coefficient emphasizes the desirability of making a conductivity test on samples used instead of assuming values. It also indicates, however, that the conductivity test can be replaced by a measurement of the temperature coefficient. It is often easier to measure the resistance between two fixed points on a sample at two known temperatures and thus obtain the temperature coefficient than to measure the specific resistance, which is in a sense an absolute measurement. A value can thus be obtained for the conductivity which is reliable, according to the present results, within one-half per cent. Four particular cases suggest themselves in which the measurement of temperature coefficient has considerable advantage over a conductivity measurement.

(*a*) *Odd shapes.*—Unless a uniform sample can be prepared, the determination of conductivity directly is hopeless. Through the temperature coefficient, the conductivity may be known for a specimen of any shape, without the danger of altering its properties by the preparation of a uniform sample.

(*b*) *Short samples.*—For very short samples, the difficulty of measurement of the dimensions and the possible uncertainty of the current distribution limit the use of conductivity measurement. Neither objection applies to the determination of the temperature coefficient.

(*c*) *Wires that have been distorted or bent.*—As shown above, the apparent conductivity of a wire that has once been distorted by bending is incorrect, while such treatment does not materially affect the temperature coefficient or the real conductivity. The temperature coefficient, therefore, gives the real conductivity better in such cases than does a direct measurement of the conductivity.

(*d*) *The estimation of chemical purity.*—The use of conductivity as a criterion of chemical purity is familiar. Evidently the temperature coefficient is fully as reliable a criterion as the conductivity, and is more generally applicable, and is often an easier test to apply than either the conductivity or chemical determinations. Indeed, the temperature coefficient is used as a criterion of purity in the selection of platinum for platinum thermometers. It is also interesting to know that the temperature coefficient is used commercially as a criterion of purity for some of the metals used in incandescent lamp manufacture; it is the most delicate test available of some of the desirable properties of the pure material, surpassing even the chemical tests, which are much more laborious.

6. EXPLANATION OF DISAGREEMENTS OF PREVIOUS OBSERVERS

We now have an explanation of the disagreements of the results of previous observers, aside from the errors of their measurements. For example, one of the most carefully established previous values, that adopted by the American Institute of Electrical Engineers, was the result of over 100 determinations made by Messrs. Robinson and Holz, of the General Electric Company. They found variations in the value and considered 0.0042 as the best that could be done in assigning a mean. As may be seen, the same conclusion could be reached from the data of this paper if the temperature coefficient only were considered. 0.0042 is the temperature coefficient, α_0, for copper of conductivity equal to 98.3 per cent. If it is used for a sample whose conductivity is 100 per cent, the error of the computed value at 100° C is over one-half per cent. (If the French coefficient is used in a similar case, the error is 2 per cent.) It is interesting to notice that the A. I. E. E. temperature coefficient happens to correspond very closely to 98 percent conductivity, which has been the conductivity usually specified for annealed copper on purchases in this country.

7. VALUES SUGGESTED FOR ANNEALED AND HARD-DRAWN COPPER

According to the results of an investigation now being carried out at the Bureau of Standards, a fair value to assume for the conductivity of good commercial *annealed* copper wire (in cases where assumption is unavoidable) is 100 per cent, for which

$$\alpha_0 = 0.00428,\ \alpha_{15} = 0.00402,\ \alpha_{20} = 0.00394,\ \text{and}\ \alpha_{25} = 0.00386$$

This value would usually apply to instruments and machines, since they are generally wound with annealed wire. Similarly, the conductivity of good commercial *hard-drawn* copper wire may be taken as 97.3 per cent, for which

$$\alpha_0 = 0.00415,\ \alpha_{15} = 0.00391,\ \alpha_{20} = 0.00383,\ \text{and}\ \alpha_{25} = 0.00376$$

IV. THE MATHEMATICAL EXPRESSION OF THE TEMPERATURE COEFFICIENT

The simple mathematical relations between the different methods of expressing the temperature coefficient are sometimes confused; it is therefore thought desirable to include a discussion of them in this paper.

1. ON GENERAL FUNCTIONS OF TEMPERATURE

The law expressing any variation with temperature may be written:

$$R_t = R_\tau f(t) \tag{1}$$

in which R_τ is a constant, τ being some standard temperature. The "temperature coefficient at t_1 °," α_{t_1}, is defined in the most general way by the following equation:

$$\alpha_{t_1} = \frac{1}{R_{t_1}}\left(\frac{dR}{dt}\right)_{t_1} \tag{2}$$

This equation applies to any variation with temperature, whether linear or not.

From (1) and (2),

$$\alpha_{t_1} = \frac{1}{f(t_1)}\left[\frac{df(t)}{dt}\right]_{t_1} \tag{3}$$

Hence, if we know f(t), we can calculate the temperature coefficient at any temperature. f(t) can usually be put in the form of a series of ascending powers of t, so that the calculation of α_{t_1} is simple. This quantity, α_{t_1} is then usable in calculating the value of R for temperatures close to the temperature of reference, t_1, (and is not, in the general case, applicable to temperatures far from t_1). Thus, from (2),

$$(dR)_{t_1} = \alpha_{t_1} R_{t_1} dt \tag{4}$$

Hence, for t not far from t_1

$$\left\{\begin{aligned} R_t - R_{t_1} &= \alpha_{t_1} R_{t_1} [t - t_1] && (5) \\ R_t &= R_{t_1}(1 + \alpha_{t_1}[t - t_1]) && (6) \end{aligned}\right.$$

(6) and (3) enable us to apply a simple linear computation to any variation with temperature for small temperature differences.

Case 1. Linear temperature coefficient.—The law of variation with temperature is

$$R_t = R_0(1 + \alpha_0 t) \tag{7}$$

or,

$$f(t) = 1 + \alpha_0 t \tag{8}$$

Hence, from (3) and (8),

$$\alpha_{t_1} = \frac{\alpha_0}{1 + \alpha_0 t_1}, \text{ or,} \tag{9}$$

$$\alpha_{t_1} = \frac{1}{\frac{1}{\alpha_0} + t_1} \tag{10}$$

Now, since $\frac{dR}{dt} = \text{constant} = \frac{R_t - R_{t_2}}{t - t_2}$,

∴ from (2)

$$\alpha_{t_2} R_{t_2} = \frac{R_t - R_{t_2}}{t - t_2}$$

$$\therefore\ R_t = R_{t_2}(1 + \alpha_{t_2}[t - t_2]) \tag{11}$$

It is to be noted that (11) is the same as (6), except that (11) has not the restriction that t be not far from t_1. We see from (11) that any temperature may be used as standard temperature[6] as well as 0° [as in (7)], and still the form of f(t) be unchanged. Thus, corresponding to (10), we have

$$\alpha_{t_1} = \frac{1}{\frac{1}{\alpha_{t_2}} + (t_1 - t_2)}, \tag{12}$$

by means of which we can obtain the ture coefficient attempera any temperature directly from its value at any other temperature.

It is sometimes convenient to use (12) in the form

$$\alpha_{t_1} = \alpha_{t_2} - \alpha_{t_2}^2 (t_1 - t_2) + \alpha_{t_2}^3 (t_1 - t_2)^2 - \ . \ . \ . \tag{13}$$

The *temperature coefficient of resistance of copper* is linear within practical limits of accuracy and of temperature, and the above formulas apply to it. As has been shown in this paper, the temperature coefficient varies for different samples of copper, and a relation of temperature coefficient to conductivity has been found. We may now write a formula giving the temperature coefficient for a sample of copper of any conductivity and at any temperature of reference. Denoting percent conductivity, expressed decimally, by n, our experimental result is

$$\alpha_{20} = n\,(0.00394) \tag{14}$$

$$\therefore \quad \alpha_{t_1} = \frac{1}{\frac{1}{n\,(0.00394)} + (t_1 - 20)} \tag{15}$$

The table given on page 81 was calculated by (15). As pointed out on page 82, the change of resistivity per degree change of temperature is independent of the temperature of reference and of the sample of copper. Hence, for reducing resistivity from one temperature to another no formulas are needed. Formulas (14) and (15) are, of course, intended to apply only to the kinds of copper and the temperature range of this paper and are believed to be reliable within one-half per cent.

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[6] The terms should not be confused: "Temperature of reference" $= t_1 =$ temperature at which we compute a temperature coefficient. "Standard temperature" $= T =$ temperature in terms of which f(t) is expressed, Eq. (1).

Case II. Two-term temperature formula.—This is the case of many resistance materials, of which manganin is an important example. The law of variation with temperature may be written:

$$R_t = R_T \, (1 + a_T \, [t-T] + b_T \, [t-T]^2) \tag{16}$$

or,

$$f(t) = 1 + a_T \, [t-T] + b_T \, [t-T]^2 \tag{17}$$

From (3) and (17),

$$\alpha_{t_1} = \frac{a_T + 2b_T \, [t_1 - T]}{1 + a_T \, [t_1 - T] + b_T \, [t_1 - T]^2} \tag{18}$$

In the case of *manganin*, *a* and *b* are very small quantities, a_{25} being usually between −0.000 01 and +0.000 03, and *b* between −0.000 000 3 and −0.000 000 5; hence we may neglect the denominator in (18) and write

$$\alpha_{t_1} = a_T + 2b_T \, (t_1 - T) \tag{19}$$

Also,

$$\alpha_{t_1} = \alpha_{t_2} + 2b_T \, (t_1 - t_2) \tag{20}$$

By means of (20) we can obtain the temperature coefficient at any temperature directly from its value at any other temperature.

Case III. Reciprocal two-term formula.—This is the case of Matthiessen's formula for the temperature coefficient of copper. The law of variation with temperature is:

$$\frac{R_t}{R_0} = \frac{1}{1 + At + Bt^2} \tag{21}$$

or

$$f\,(t) = \frac{1}{1 + At + Bt^2} \tag{22}$$

From (3) and (22),

$$\alpha_{t_1} = \frac{-A - 2Bt_1}{1 + At_1 + Bt_1^2} \tag{23}$$

The values of A and B in Matthiessen's formula for copper are −0.0038701 and +0.000009009, respectively. Substituting these values in (23), we find for α_0 and α_{20}:

$$\alpha_0 = +0.003870, \; \alpha_{20} = +0.003789 \tag{24}$$

"Matthiessen's temperature coefficient for 0° to 20°," as given on page 70, is quite a different thing from the temperature coefficient *at* a given temperature, as above discussed. The value there considered (page 70) is simply:

$$\alpha_{(0\text{ to }20)_0} = \frac{R_{20}-R_0}{20\,R_0} = \frac{\frac{R_{20}}{R_0}-1}{20} = +0.003984$$

$$\alpha_{(0\text{ to }20)_{20}} = \frac{R_{20}-R_0}{20\,R_{20}} = \frac{1-\frac{R_0}{R_{20}}}{20} = +0.003690$$

This pair of values simply reduces from 0° C to 20° C and from 20° C to 0° C and applies to no other temperature interval. Not only is the use of this temperature coefficient thus restricted, but the temperature coefficient at particular temperatures, as calculated in (24), is restricted to infinitesimal temperature differences; accordingly we see that it is impossible to use Matthiessen's formula in general without employing the awkward form in which it is expressed.

2. CALCULATION OF LINEAR TEMPERATURE COEFFICIENT FROM OBSERVATIONS

α_{t_1} from observations at t_1 and one other temperature, t.
From (11),

$$\alpha_{t_1} = \frac{R_t - R_{t_1}}{R_{t_1}\,(t-t_1)} \tag{25}$$

α_{t_1} from observations at any two temperatures, t and s.
Applying (25), we deduce

$$\alpha_{t_1} = \frac{R_t - R_s}{R_s(t-t_1) - R_t(s-t_1)} \tag{26}$$

"Differential α_{t_1}" from observations at t_1 and one other temperature, t. The "differential α_{t_1}" is the temperature coefficient obtained when a copper sample is measured against another in the same bath and thus undergoing the same variations of temperature. It is simply the difference of the temperature coeffi-

cients of the two samples. Thus, using α' and R' for one sample, and α and R for the other,

$$\alpha'_{t_1}-\alpha_{t_1}=\frac{R'_t-R'_{t_1}}{R'_{t_1}-(t-t_1)}-\frac{R_t-R_{t_1}}{R_{t_1}(t-t_1)}=\frac{\frac{R'_t}{R_t}-\frac{R'_{t_1}}{R_{t_1}}}{\frac{R'_{t_1}}{R_{t_1}}(t-t_1)}$$

Let r denote the quantity $\frac{R'}{R}$, which is measured in each case.

$$\therefore \alpha'_{t_1}-\alpha_{t_1}=\frac{r_t-r_{t_1}}{r_{t_1}(t-t_1)} \tag{27}$$

"*Differential* α_{t_1}" *from observations at any two temperatures*, t *and* s. When α'_{t_1} and α_{t_1} are nearly the same, as is the case with samples of refined copper, the following approximation applies, deduced from (26),

$$\alpha'_{t_1}-\alpha_{t_1}=\frac{r_t-r_s}{r_s(t-s)} \tag{28}$$

[The *differential method* of determining temperature coefficients is applicable to any form of temperature variation. Applied to the measurement of the temperature coefficients of manganin resistance standards, it has been in use for several years at the Bureau of Standards. The computations are facilitated by the fact that the observed resistance changes are small, and only a low accuracy is required in the measurement of temperature.]

2. EFFECT OF THERMAL EXPANSION IN THE EXPRESSION OF THE LINEAR TEMPERATURE COEFFICIENT

The temperature coefficient of resistance is measured by observations of resistance and temperature. Since the dimensions change with temperature, evidently the temperature coefficient of resistivity or specific resistance can not be directly obtained. As it is sometimes desirable to express these temperature coefficients, the relations are given here.

The temperature coefficient considered up to this point is that ordinarily used; it is the temperature coefficient of resistance as measured between potential terminals rigidly attached to the wire (such as the soldered terminals used in the work of this paper). It may be defined by Eq. (7), viz:

$$R_t = R_0(1 + \alpha_0 t) \tag{7}$$

and may be called the *"constant mass" temperature coefficient of resistance.*

We shall now use a new set of subscripts for α, using 0° as the standard temperature throughout. Let:

α_R = *"constant mass" temperature coefficient of resistance.*
α_ρ = *"constant volume" temperature coefficient of resistivity.*
α_δ = *temperature coefficient of meter-gram resistivity.*
α_K = *"knife-edge" temperature coefficient of resistance.*
l = length.
s = sectional area.
ρ = resistance per cm cube $= \frac{\mathrm{Rs}}{\mathrm{l}}$
m = mass
δ = resistance per meter-gram $= \frac{\mathrm{Rm}}{10\,000\mathrm{l}^2}$
γ = coefficient of linear expansion.

Rewriting (7), which defines the *"constant mass" temperature coefficient of resistance,*

$$R_t = R_0(1 + \alpha_R t) \tag{29}$$

The *"constant volume" temperature coefficient of resistivity* may be defined by:

$$\rho_t = \rho_0(1 + \alpha_\rho t) \tag{30}$$

Now, $$R_t = \frac{\rho_t l_t}{s_t} = \rho_0(1 + \alpha_\rho t)\frac{l_t}{s_t} = \frac{\rho_0 l_0}{s_0}(1 + \alpha_\rho t)(1 - \gamma_w t)$$

where γ_w is the coefficient of linear expansion of the wire. Since γ is a very small quantity we may write:

$$R_t = R_0(1 + [\alpha_\rho - \gamma_w]t) \tag{31}$$

From (29) and (31),

$$\alpha_R = \alpha_\rho - \gamma_w \tag{32}$$

The *temperature coefficient of meter-gram resistivity* may be defined by:

$$\delta_t = \delta_o(1 + \alpha_\delta t) \qquad (33)$$

Now, $$R_t = \frac{10\,000\,\delta_t l_t^2}{m} = \frac{10\,000\,\delta_o l_o^2}{m}(1 + \alpha_\delta t)\,(1 + 2\gamma_w t)$$

$$\therefore R_t = R_o(1 + [\alpha_\delta + 2\gamma_w]t) \qquad (34)$$

From (29) and (34),

$$\alpha_R = \alpha_\delta + 2\gamma_w \qquad (35)$$

The "*knife-edge*" *temperature coefficient of resistance*, α_K, is that measured between knife-edges mounted on some support. The result obtained depends on the material of the support. α_K is therefore not a true property of the metal, but the difference is very small. α_K may be defined by the following equation, l representing length in terms of the distance between the knife edges.

$$\left(\frac{R}{l}\right)_t = \left(\frac{R}{l}\right)_o(1 + \alpha_K t) \qquad (36)$$

Now, $$R_t = \left(\frac{R}{l}\right)_t l_t = \left(\frac{R}{l}\right)_o l_o\,(1 + \alpha_K t)\,(1 + [\gamma_w - \gamma_b]t),$$

where γ_b is the coefficient of linear expansion of the base which supports the knife edges.

$$\therefore R_t = R_o\,(1 + [\alpha_K + \gamma_w - \gamma_b]t) \qquad (37)$$

From (29) and (37),

$$\alpha_R = \alpha_K + \gamma_w - \gamma_b \qquad (38)$$

If the base which supports the knife edges is made of the same metal as the wire under observation, (38) becomes

$$\alpha_R = \alpha_K \qquad (39)$$

If the base is made of some material whose length does not change with temperature, such as invar, (38) becomes

$$\alpha_R = \alpha_K + \gamma_w \qquad (40)$$

These values of α_K and α_R are intermediate between the values of α_ρ and α_δ. α_R and α_K are quantities which can be directly measured; α_ρ and α_δ are calculated from one of them. The four values are defined in (29), (30), (33), and (36), and their interrelations are given in (32), (35), and (38).

The four α's are identical for most practical purposes; e. g., for an α_R of copper equal to 0.00428, α_δ (which is the α farthest different from α_R) = 0.00425. These differences in the α's are very much less than the variations among different samples and different temperatures of reference. When precision work requires that one of the four α's be specified, the Bureau of Standards prefers the use of α_R, which is that directly measured when soldered potential terminals are used, and most nearly corresponds to practical use.

V. SUMMARY

1. The foregoing investigation shows that, for representative samples of the copper at present furnished for electrical use, the *conductivity and temperature coefficient are proportional,* to a high degree of accuracy for differences in physical condition, and to a fair accuracy for differences in chemical composition of samples.

2. This relation may be put in the following very convenient form for reducing the results of resistivity measurements to a standard temperature: *The change of the resistivity per degree C of a sample of copper is 0.000598 ohm per meter-gram, or 0.00681 micro-ohm per centimeter cube.*

3. The distortions caused by bending and winding a wire are shown to produce no material change in the temperature coefficient; so that the temperature rise in machines and instruments may be calculated from measurements of the resistance of the windings with greater confidence than heretofore.

4. The measurement of temperature coefficient is shown to present an advantageous substitute for the direct measurement of conductivity in a number of cases.

5. A discussion is given of the mathematical relations between the different methods of expressing the temperature coefficient.

WASHINGTON, July 12, 1910.

VI. APPENDIX.—REICHSANSTALT RESULTS

The bureau has just received from Doctor Warburg, president of the Physikalisch-Technische Reichsanstalt, Germany, a table of results on resistivity and temperature coefficient of copper samples. This table was prepared by Professor Lindeck in February, 1910, but has not been published. These results furnish a remarkable corroboration of those obtained here, and permission has been kindly given to publish them herewith. They represent measurements made over a period of five years on various forms of copper samples. They are of especial interest, as they include a great range of conductivity. The table is given below, Table III. The results have also been reduced to the same form of expression as the preceding data of this paper, and as thus reduced are given in Table IV, in the same order as in Table III.

TABLE III

Results obtained on the resistivity and temperature coefficient of copper at the Reichsanstalt

Resistance test No.	Form of specimen (W—wire) (S—sheet) (T—trolley) (C—cable)	Cross section in sq. mm.	Density, d	Temperature coefficient at 15° C, α_{15}	Specific resistance; ohm, meter, sq. mm. at 15° C, ρ'_{15}	Product $(\alpha_{15})(\rho'_{15})(10)^7$
1-1905	C 12	40.	8.90_6	0.00400	0.0168_7	675
	C 19	40.	8.92_6	402	168_3	677
5-1905	C 37	400.	8.89_2	401	168_9	677
43-1905	T	60.96	8.88_2	393	172_8	679
98-1905	W	0.379	8.85_8	395	169_2	668
	W	1.751	8.88_1	402	168_9	679
	W	3.703	8.92_3	399	168_7	673
	W	12.54	8.89_4	400	168_8	675
143-1905	W	1.534	8.82_5	393	174_7	687
1-1906	C 19	95.	8.91_1	395	170_2	672
43-1906	C 19	50.	8.82_8	394	173_9	685
78-1906	S	15.×4	8.85_4	134	522_8	701
	S	15.×2	8.86_0	135	519_4	701
137-1906	W	0.8281	8.94_4	293	228_3	669
	W	0.8295	8.94_3	291	229_4	668
138-1906	W	7.113	8.84_0	393	173_9	683
	W	7.170	8.87_5	404	168_2	680

TABLE III—Continued

Results obtained on the resistivity and temperature coefficient of copper at the Reichsanstalt

Resistance test No.	Form of specimen (W=wire) (S=sheet) (T=trolley) (C=cable)	Cross section in sq. mm.	Density, d	Temperature coefficient at 15° C, α_{15}	Specific resistance; ohm, meter, sq. mm. at 15° C, ρ'_{15}	Product $(\alpha_{15})(\rho'_{15})(10)^7$
200-1906	C 19	102.3	(8.88_5)	0.00396	0.0171	...
	W	50.39	8.90_4	399	169_3	676
	W	37.81	8.89_3	398	171_0	681
	W	28.29	8.88_6	401	169_5	680
	W	12.62	8.91_6	370	182_1	674
36-1907	W	24.85	8.86_8	397	171_8	682
	W	24.85	8.86_9	395	171_8	679
36-1907	W	24.81	8.87_6	395	171_4	677
	W	24.86	8.86_8	396	171_8	680
	W	24.87	8.85_6	396	172_4	682
	W	25.28	8.86_8	389	172_3	670
	W	24.89	8.86_4	392	171_8	673
	W	25.03	8.86_1	397	172_6	684
	W	25.34	8.86_8	396	171_9	681
	W	25.21	8.86_5	396	172_4	683
192-1907	W	0.8043	8.88_8	407	167_9	683
74-1908	W	25.34	8.86_2	389	175_1	681
77-1908	W	35.70	8.85_7	401	170_5	684
79-1908	W	19.64	8.91_6	388	173_7	674
	W	17.40	8.91_3	291	235_4	685
	W	19.53	8.91_8	259	269_3	697
	W	20.56	8.89_4	316	215_4	681
	W	3.264	8.92_6	394	170_5	672
	W	7.332	8.93_0	289	235_6	681
	W	7.249	8.91_9	281	241_8	679
	W	7.517	8.89_5	282	241_1	680
2-1909	W	0.7836	8.93_2	203	337_8	686
	W	0.7821	8.92_6	200	341_4	683
11-1909	S	60.×5	....	149	475_4	708
12-1909	W	78.59	8.92_4	396	169_3	670
	W	78.57	8.92_0	397	169_2	672
35-1909	W	0.7667	8.92_0	230	299_7	689

The mean value of *C*, Table IV, for the 48 samples is 0.00395_0. For the 34 samples of conductivity above 94%, the mean value of *C* is 0.00393_6. This agrees very well with the mean value 0.00393_8 found in the present investigation, in which all of the samples were of conductivity above 94%. For the 14 Reichsanstalt samples of low conductivity, varying from 32.8% to 92.5%, *C* varied irregularly between 0.00390 and 0.00406. The maximum departure from the mean value, 0.00394, is seen to be 3%, a remarkably close agreement for such a wide range of conductivity. This is of particular interest to those who work with impure copper of low conductivity. For this result shows that the measurement of conductivity may be replaced by the measurement of temperature coefficient, with an accuracy sufficient for commercial purposes, even when the conductivity is as low as one-third that

TABLE IV

Reichanstalt results reduced to the form of expression used in Table I

Ohms per metergram at 20° C, δ_{20}	Percent conductivity, n_δ	Temperature coefficient at 20° C, δ_{20}	C
.15313	99.93	0.00392_8	0.00392_6
.15325	99.85	394_1	394_7
.15319	99.89	393_1	393_6
.15649	97.78	385_4	394_1
.15287	100.10	387_8	386_9
.15299	100.02	394_1	394_0
.15352	99.68	391_2	392_5
.15312	99.94	392_3	392_4
.15716	97.37	385_4	395_8
.15466	98.94	387_8	391_4
.15651	97.77	386_4	395_3
.46588	32.85	133_1	405_3
.46318	33.04	134_1	405_9
.20718	73.86	288_6	391_6
.20814	73.52	286_8	390_1
.15672	97.64	385_4	394_7
.15227	100.49	396_0	394_1
.15492	98.77	388_2	393_1
.15373	99.54	391_2	393_0
.15506	98.69	390_2	395_4
.15364	99.60	393_1	394_7
.15535	92.54	363_2	392_6
.15534	98.51	389_3	395_2
.15536	98.50	387_2	393_3

TABLE IV

Reichanstalt results reduced to the form of expression used in Table I

Ohms per metergram at 20° C, δ_{20}	Percent conductivity, n_δ	Temperature coefficient at 20°C, α_{20}	C
.15516	98.62	0.00387_3	0.00392_7
.15534	98.51	388_3	394_2
.15567	98.30	388_3	395_0
.15575	98.25	381_6	388_4
.15531	98.53	384_5	390_2
.15558	98.36	389_3	395_8
.15543	98.45	388_3	394_4
.15582	98.20	388_3	395_4
.15214	100.58	398_9	396_6
.15816	96.75	381_6	394_4
.15400	99.36	393_1	395_6
.15776	97.00	380_6	392_4
.21292	71.87	286_8	399_1
.24315	62.93	255_7	406_3
.19457	78.65	311_1	395_6
.15523	98.58	386_4	392_0
.21329	71.74	284_9	397_1
.21865	69.98	277_1	396_0
.21745	70.37	278_1	395_2
.30471	50.22	200_9	400_0
.30752	49.76	198_0	397_9
.15407	99.32	388_3	391_0
.15392	99.42	389_3	391_6
.27059	56.55	227_4	402_1
$\delta_{20}=(\rho'_{15})(d)+0.00299$	$n_\delta=\frac{0.153022}{\delta_{20}}$	$\alpha_{20}=\frac{a_{15}}{1+5a_{15}}$	$C=\frac{\alpha_{20}}{n_\delta}$

of pure copper. It might be mentioned that Lagarde,[7] in 1888, found that for samples composed of 98% copper and 2% tin, whose conductivity was one-third that of pure copper, the constant, *C*, was within 7% of *C* for pure copper.

While all of the foregoing results for *C*, on samples of very low up to the highest conductivity, show a good agreement to commercial accuracy, the range of 94% to 101% conductivity is found at the Bureau of Standards to show a much closer agreement. For this range, which includes the good commercial copper furnished for use as electrical conductors, the average deviation of *C* from the mean value 0.00393_8 is only 0.00000_8, or 0.2%. Also, when the conductivity and temperature coefficient are altered by annealing or hard-drawing, *C* has been found to remain constant within the experimental error.

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[7] Ann. Tél. **15**, 409; 1888.

Attention is called to the column of densities in the table of results obtained at the Reichsanstalt. The mean value is 8.89_0. This is the same as the value in use in the Bureau of Standards and very widely elsewhere. It is hoped that this agreement in the results for temperature coefficient and density will assist in making possible an early international agreement on copper standards.

WASHINGTON, November 29, 1910.

THE ELECTRICAL CONDUCTIVITY OF COMMERCIAL COPPER

By F. A. Wolff and J. H. Dellinger

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I. INTRODUCTION

The values in use for the conductivity, resistivity, and temperature coefficient of copper vary considerably. The standard values for annealed copper as used by various institutions in different countries are given in Table I, on the adjoining page:

1. NOTES ON TABLE OF STANDARD VALUES

The values given in the table for the various temperatures are computed from the values at the particular standard temperature, which are indicated by heavy-faced type. In each column the temperature coefficient of that column is used in computing the resistivity in ohms per meter-gram at the various temperatures.

The data for the English values (col. 1) were obtained from the report of the Engineering Standards Committee, August, 1904.

The values for "Normal Kupfer" (col. 2) were computed from the data given in E. T. Z. 17, 402; 1896, and "Normalien, etc., d. Verbandes Deutscher Elektrotechniker," 1907, page 68. The value for conductivity given was reduced to meter-gram resistivity by the use of the density given as standard, 8.91. The values in column 3 are calculated on the assumption of a density of 8.89. The German "Normal Kupfer" is in use also in Austria.

The Matthiessen value as computed by Lindeck (col. 4) is based on the data given in C. Hering's "Conversion Tables" (John Wiley and Sons, N. Y., 1904), page 104, and was reduced to the meter-gram basis on the assumption of the density, 8.89, and Matthiessen's temperature formula.

The values which were adopted by the American Institute of Electrical Engineers in 1893 are given in col. 5. They were derived from the results Matthiessen published in 1862. (The 0° and 20° meter-gram values are equivalent to 1.59425 and 1.72128 micro-ohms per cm cube, respectively). In 1908 Matthiessen's temperature formula was dropped by the A. I. E. E. and the linear temperature coefficient of 0.0042 at 0° C was adopted (col. 6); this vitiated the old wire table of the Institute; and, as the 0° value of the resistivity was retained, the resistivity at all other temperatures was altered. The 20° value of the resistivity was retained by the Bureau of Standards (since the measurements of Matthiessen at 20° C were probably at least as

TABLE I

Standard Values for the Resistivity, Temperature Coefficient, and Density of Annealed Copper

Temperature C	1 England (Eng. Stds. Com., 1904)	2 Germany, "Normal Kupfer," density 8.91	3 Germany, "Normal Kupfer," assuming density 8.89	4 Lindeck, Matthiessen value, assuming density 8.89	5 A. I. E. E. before 1908 (Matthiessen value)	6 A. I. E. E. after 1908	7 Bureau of Standards before July 1, 1910	8 Bureau of Standards after July 1, 1910
	RESISTIVITY IN OHMS PER METER-GRAM							
0°	0.14136_8	0.13959_0	0.13927_7	0.14157_1	0.14172_9	0.14172_9	0.14116_4	0.14106_8
15°	$.15043_7$	$.14850_0$	$.14816_7$	$.14997_4$	$.15014_1$	$.15065_8$	$.15005_8$	$.15003_4$
(15.6°)	.1508							
20°	$.15346_8$	$.15147_0$	$.15113_0$	$.15285_1$	$.15302_3$	$.15363_4$	$.15302_2$	$.15302_2$
25°	$.15648_9$	$.15444_0$	$.15409_4$	$.15576_8$	$.15593_8$	$.15661_0$	$.15598_6$	$.15601_0$
	TEMPERATURE COEFFICIENT							
0°	0.00428	0.00425_6	0.00425_6	(1)	(1)	0.0042	0.0042	[2](0.00427_7)
15°	$.00402_3$	.004	.004			$.00395_1$	$.00395_1$	[2]($.00401_0$)
20°	$.00394_3$	$.00392_2$	$.00392_2$			$.00387_6$	$.00387_6$	[2](.00394)
25°	$.00386_5$	$.00384_6$	$.00384_6$			$.00380_1$	$.00380_1$	[2]($.00386_4$)
	DENSITY							
	8.89	8.91	(8.89)	(8.89)	8.89	8.89	8.89	[3]8.89

---

[1] Matthiessen's formula.

[2] This temperature coefficient applies only to this particular resistivity. The temperature coefficient is considered to be proportional to conductivity. Expressed otherwise, the change of *resistivity* per degree C is considered to be a constant, viz, 0.000598 ohm per meter-gram.

[3] This is the density at 20° C. It corresponds to 8.90 at 0° C.

reliable as those at lower temperatures; and since the 20° value was the one in practical use even on the old basis); and the temperature coefficient of 0.0042 at 0° C was adopted (col. 7).

Since a more accurate value for the temperature coefficient has been obtained at the Bureau of Standards, it has been applied to give the values in col. 8, which represent the present practice of the Bureau.

3. SCOPE OF THIS INVESTIGATION

The foregoing table makes evident the need for data to be used in establishing more reliable standard values. The matter of obtaining such data having been submitted to the Bureau of Standards by the American Institute of Electrical Engineers, an investigation has been made of the copper furnished for electrical uses. The cooperation of a number of the important refiners and manufacturers of copper wire was secured. These companies furnished samples for measurement and information regarding their material and their practices. Incidental to the investigation of copper it was thought desirable to secure some data on aluminum, and accordingly the cooperation of the chief producer of aluminum was also secured. The companies whose material was represented in the investigation were the following:

Smelters	Calumet and Hecla Smelting Works, Hubbell, Mich.
	Quincy Mining Co., Hancock, Mich.
	Buffalo Smelting Works, Buffalo, N. Y.
Electrolytic Refiners.	American Smelting and Refining Co., Maurer, N. J.
	The Baltimore Copper Smelting and Rolling Co., Baltimore, Md.
	The U. S. Metals Refining Co., Chrome, N. J.
	Raritan Copper Works, Perth Amboy, N. J.
	Nichols Copper Co., Laurel Hill, N. J.
	A. Grammont, Pont-de-Chéruy, France.
Wire Manufacturers.	American Brass Co., Waterbury, Conn.
	John A. Roebling's Sons Co., Trenton, N. J.
	Standard Underground Cable Co., Perth Amboy, N. J.
	Heddernheimer Kupferwerk und Süddeutsche Kabelwerke, Frankfurt am Main, Germany.
	Kabelfabrik-und Drahtindustrie-Actien-Gesellschaft, Vienna, Austria.
Aluminum Wire Manufacturer.	Aluminum Company of America, Pittsburg, Pa.

Eleven of these companies kindly furnished samples and information at the request of the Bureau of Standards, and the Bureau desires hereby to express its thanks and appreciation for their assistance. Samples of the products of the other four companies were obtained in other ways. Particular thanks is due Mr. W. H. Bassett, of the American Brass Company, who has taken great interest in the work, and who has contributed a valuable set of data on conductivity; and to Mr. Wm. Hoopes, of the Aluminum Company of America, who furnished valuable data on aluminum; and to Mr. E. A. C. Smith, of the Baltimore Copper Smelting and Rolling Company, who supplied valuable information and a quantity of specially refined cathode copper. The authors desire also to express their appreciation of the assistance of Mr. E. E. Weibel, who made some of the measurements.

A considerable number of the most important refiners and manufacturers of copper wire in this country are included in the above list; Germany, France, and Austria are each represented by one company. Since most of the world's copper is refined in this country, and the results of the measurements on the foreign samples showed no particular difference from the American samples, all the results will be given without distinguishing the foreign from the American product. The various companies were asked to furnish representative samples of their regular commercial product, both hard-drawn and annealed, and from two to twenty samples were received from each. It is not believed that the measurements made upon the few samples from each company indicate accurately the average of the product of that company, but it is considered that the mean of all the measurements indicates very well the average of the present copper of commerce. The results are given below. Results are also given for measurements on a few aluminum wires, together with the data on aluminum furnished by the Aluminum Company of America.

An effort was also made to determine what was the highest conductivity obtainable without extraordinary experimental precautions and expense, and the measurements made upon a few samples of copper of especially high conductivity are, therefore, also given. It was considered desirable also to make a complete investigation of the effect upon the conductivity of drawing to progressively smaller sizes, and to study the question of annealing, but these two matters have had to be dropped because of the pressure of other work; it is hoped that they can be taken up at a later time.

II. THE EXPERIMENTAL WORK

The samples upon which measurements were made were wires Nos. 6 to 18, B. and S. gage, about 120 cm in length. Most of the samples were No. 12. The resistivity in ohms per meter-gram and percent conductivity were computed from measurements of the length, mass, and resistance. The resistivity in ohms per meter-gram is the product of the resistance per meter and the mass per meter. The percent conductivity is computed by dividing 0.153022 by the resistance per meter-gram at 20° C. (This figure is the value assumed by the Bureau of Standards as representing the "Matthiessen Standard" at 20° C. It corresponds to 1.72128 micro-ohms per centimeter cube at 20° C, on an assumed density of 8.89.) The Thomson bridge method was used for measuring the resistances, and an accuracy of 0.01 percent was easily attained. The resistance of the copper sample was compared with the resistance of a copper standard in the same bath as the test sample, thus eliminating the necessity of very accurate temperature measurement. The resistances of the copper standards were carefully checked from time to time against manganin standards; in these measurements, of course, temperature as well as resistance had to be measured accurately. The accuracy of the resistivity and conductivity values obtained is believed to be within 0.03 percent, a limit determined chiefly by the uncertainty of the total length measurement (many of the wires were not entirely free from small bends) and the lack of uniformity of cross-section of the wires.

1. THE THOMSON BRIDGE METHOD

The Thomson bridge method was first described by Sir Wm. Thomson,[4] in 1862. Hence it is called the "Thomson bridge" or "Kelvin double bridge." A diagram of the connections is given in Fig. 1. *A* and *B* are the low resistances to be compared. 5 and 7, 10 and 1, are the "branch points" or "potential points" between which are the resistances considered. *a*, *na*, *a'*, and *n'a'* are ratio arms of relatively high resistance. The theory of the method may be understood from Fig. 2. This figure represents a simple Wheatstone bridge. The simple bridge can not be used for low resistances, because the connecting resistance between *A* and *B* introduces an error if the galvanometer is connected to any

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[4] Phil. Mag. **24**, 149; 1862.

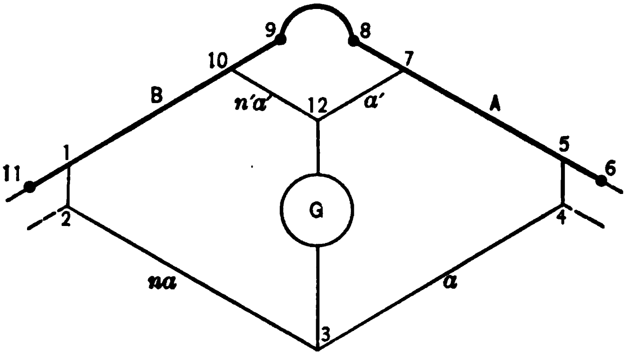

Fig. 1

of the points 7, 8, 9, or 10. (The resistances $\overline{7\ 8}$ and $\overline{9\ 10}$ are the resistances of the adjacent "current terminals" of *A* and *B*. The resistance between 8 and 9 is the "link" connecting *A* and *B*.)

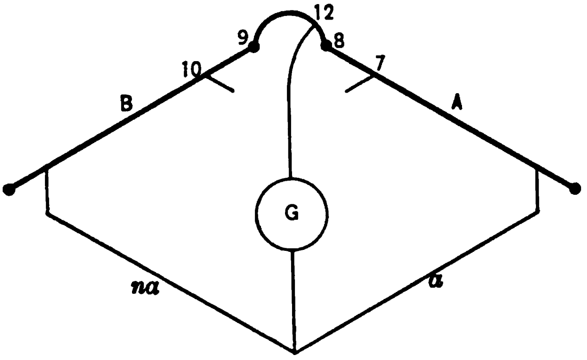

Fig. 2

However, if it were possible to bring the galvanometer lead in at some point 12 such that

$$\frac{\overline{10\ 12}}{\overline{12\ 7}}=\frac{B}{A} \tag{1}$$

since, for zero deflection of the galvanometer,

$$\frac{B+\overline{10\ 12}}{A+\overline{12\ 7}}=\frac{na}{a} \tag{2}$$

we have, for a bridge balance,

$$\frac{B}{A}=n \tag{3}$$

The equivalent of this is accomplished in the Thomson bridge by shunting $\overline{10\ 7}$ with a relatively high resistance, connecting the galvanometer to a point, 12, Fig. 1, and adjusting $n'a'$ or a' so that

$$\frac{n'a'}{a'}=\frac{B}{A}$$

The best method of accomplishing this adjustment (first published by J. H. Reeves[5]) is to remove the link, $\overline{8\ 9}$, thus reducing the bridge to a simple Wheatstone bridge, and vary a' or $n'a'$ for a galvanometer balance. Then $n=n'$. The link is then replaced, and the main ratio, $na:a$, adjusted until a galvanometer balance is attained. The "link-out" balance is, of course, disturbed by this adjustment, unless $(n'a':a')$ is varied simultaneously with $(na:a)$. It is preferable to have the "auxiliary ratio," $n'a':a'$, similar to the main ratio, and to vary them simultaneously for the "link-in" balance; thus the "link-out" adjustment is not disturbed. A double set of ratio coils frequently used is the O. Wolff type, and it was used in the work of this paper. If, however, the main and auxiliary ratios can not be varied simultaneously, the "link-in" balance may be made by varying the main ratio, then the link is taken out and the balance restored by varying the auxiliary ratio, and then the link is replaced and the main ratio again varied, and so on by successive approximations until both balances are made.

The variation of a' or $n'a'$ for the "link-out" balance may be accomplished by means of a variable resistance in series with a' or $n'a'$, at 7 or 10. A very satisfactory form for this variable resistance is a small glass tube of mercury, the resistance between the ends of which can be varied by changing the depth to which an amalgamated copper wire is immersed in it. If the range of the mercury resistance is insufficient, a manganin wire, with sliding clamp contact, may be put in series with it. Another method for obtaining the "link-out" balance is to have a slide-wire between a' and $n'a'$, along which moves the galvanometer contact.

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[5] Proc. Phys. Soc., London, **14**, p. 166; 1896.

The connecting resistances between the branch-point, 1, and the end of *na*, 2, and between 5 and 4, are usually not negligible. One method of procedure is to shift the battery leads from their normal points of connection, 6 and 11, to 4 and 2, with the link out, and measure the change of balance of the bridge by varying one of the four ratio arms. The connecting resistances are then calculated from the change of balance. The variation of one of the ratio arms to measure the change of balance may be accomplished by shunting or by varying a series resistance. In the work of this paper a small series resistance was placed in one arm, say a', the total resistance of the arm having the fixed value, 100 ohms. The small series resistance could be put in circuit or out by means of a plug, and was normally out of circuit. When the link-out balance had been made, this series resistance was put in circuit and the galvanometer deflection noted. The deflection corresponding to a given change of balance of the bridge being thus known, the change of balance caused by shifting the battery leads was obtained by observing the deflection caused by the shift, and thence the correction to the ratio, $na:a$, easily calculated. The connecting resistances between 1 and 2 and between 4 and 5 are often neglected by users of the Thomson bridge. Since they are frequently appreciable (often including the resistance of a knife-edge contact), and also since the method of this paragraph permits the correction to be readily determined, they should not be neglected.

A different method of using the Thomson bridge is to have fixed ratio arms and a variable low resistance standard. The method of measurement described above, or an equivalent method, should, however, be followed throughout, except that the link-in balance is made by varying the standard (which would be in the arm A or B) instead of by varying the ratio arms.

2. THE APPARATUS

The apparatus used in the resistance measurements consisted of an Otto Wolff "double bridge" and a special apparatus for mounting the wires under measurement. This special apparatus was designed by the authors, and it was constructed and the details of design were worked out by the Leeds and Northrup

Company. It consisted essentially of a rectangular oil bath provided with means for temperature control, and a base with electrical connections to the wire under measurement. A photograph of the apparatus is given herewith. The base upon which wires were mounted was a piece of marble, 121 cm long and 22 cm wide. The bath was provided with pipes for the flow of cooling water, and with electric heating coils and lamps, all placed beneath the marble base. An efficient thermoregulator was provided, similar in general to those described in this Bulletin **4**, p. 34; 1907. The "bulb" of this thermoregulator consisted of 500 cm of copper tubing passing around the bath in two turns, as may be seen from the photograph. A motor-driven propeller forced the oil through a vertical tube at one end of the bath, and thus produced a circulation of the oil in one direction over the marble, and in the opposite direction under the marble. The wire sample was held by heavy screw clamps at the ends of the base. The test current was passed through the wire by means of these clamps. The potential connections were steel knife-edges which were mounted rigidly 1 meter apart on the marble base. Between the knife-edges a row of small hard rubber blocks served to support the wire sample. Spring pressure devices, pressing from above, kept the wire in contact with the fixed knife-edges. A movable knife-edge was also provided, traveling along a steel scale graduated for 103 cm. Its contact pressure is adjusted by a lever and weights. This knife-edge makes it possible to measure the resistance of a sample of any length. Its position is capable of fine adjustment by a cone and socket device, and is readable by means of a vernier to 0.1 mm.

On account of the advantages of measuring samples against a standard of the same material in the same bath, frames for auxiliary copper standards were provided. These standards were wires about a meter long, with soldered potential terminals. Such a standard was placed in a frame, with its ends connected into small clamps, and its potential leads connected to binding posts. The two clamps and the two binding posts terminated in amalgamated copper rods. Mercury cups in the marble base were so placed as to receive these amalgamated terminals. When the frame was in place, the auxiliary copper standard lay parallel to

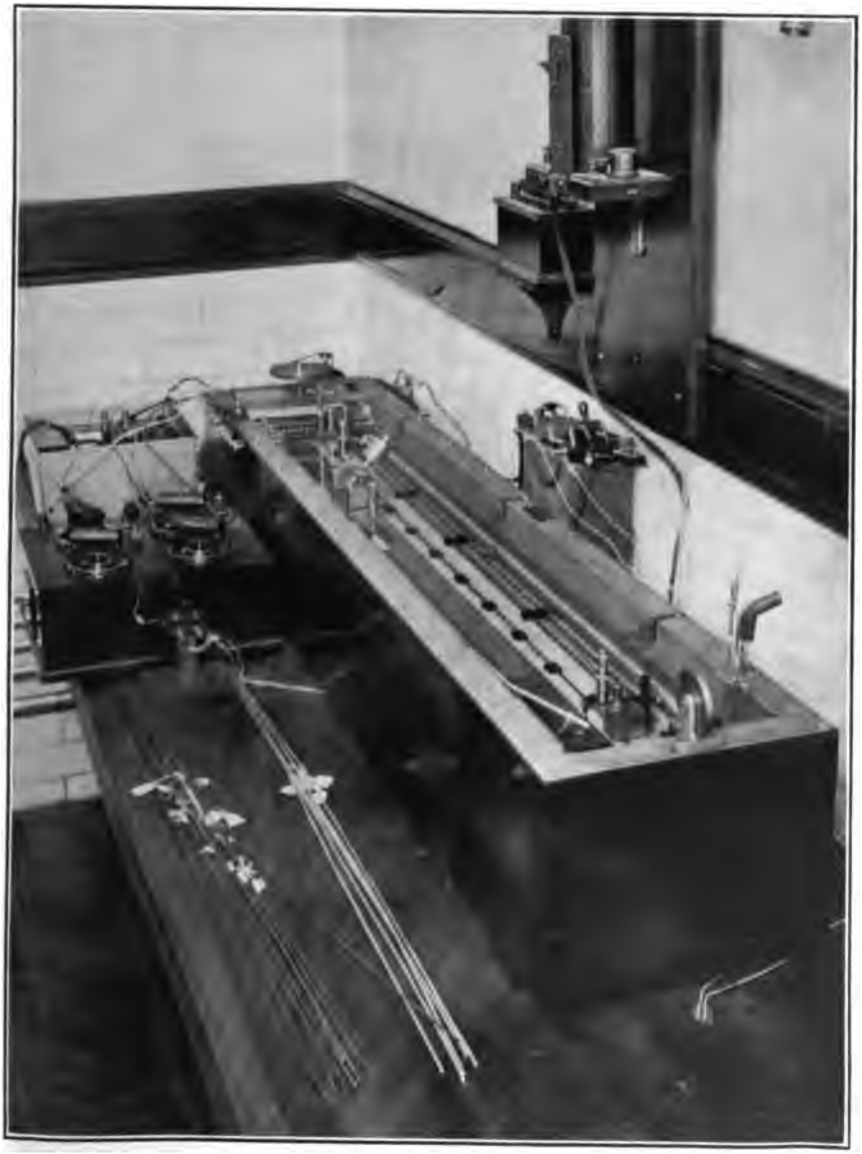

Fig. 3. *Conductivity Apparatus.*

the wire sample under measurement. The wire sample could be put into connection either with the auxiliary copper standard or with a manganin standard in a separate bath, by means of a movable amalgamated copper link. All connections were carried under the marble to binding posts on one side of the apparatus.

The apparatus was provided also with means for applying a known tension to the wire under measurement. This consisted of a pair of pulleys at one end of the bath, with a pan and weights for attaching to a cord clamped to one end of the wire sample. The effect of tension has to be considered when measuring the resistances of small wires. Experiments showed that for an increase of tension of 1 kilogram per mm^2 cross section, the resistance increased 0.025 percent, which corresponds to an increase of specific resistance of 0.011 percent. For example, if a No. 18 wire is under a tension of 1 kilogram, its resistance is 0.030 percent greater than if no tension is applied.

III. RESULTS OBTAINED

1. RESISTIVITY OF COMMERCIAL COPPER

The resistivity and percent conductivity of 89 copper wires are given in Table 2. The results are separated into groups, each group representing one company's samples. The order in which the groups are placed has no relation to the order in which the names of the companies are given on page 106. It is not desired that the few samples from each company be considered an adequate basis of judging the output of the company, although the final mean is believed to be a good indication of the average output of all.

In general, the conductivity of the annealed wires did not differ with the size of the wire, but in the case of the hard-drawn wires there were well-defined differences. (N. B.: The No. 10 wires are considered together with the No. 12 throughout, there being no appreciable difference.) In each group, accordingly, the mean of all the annealed wires is taken, and for the hard-drawn wires the mean of each size of wire in the group is taken.

The mean of the 14 group means for the annealed wires is:

Resistivity in ohms per meter-gram at 20° C = 0.15292
Percent conductivity = 100.07%

The average deviation from these means was 0.26%, and the maximum deviation of any group was 0.81%.

Values for annealed and hard-drawn wires being placed on the same line indicates that they are from the same lot of material, and should therefore correspond. In calculating "Annealed minus Hard-Drawn, Mean Percent Conductivity," col. 10, the mean of the particular size of wire in the group is taken.

For the No. 6 wires, the mean difference, annealed minus hard-drawn, is 2.30%.

For the No. 12 wires, the mean difference was 2.68%, with a mean deviation of 0.14%. Inasmuch as one company's samples were all hard-drawn and two companies' all annealed, these differences for corresponding groups do not include all the No. 12 wires. The mean difference might, therefore, also be computed in another way; taking the difference between the mean of all the annealed wires and the mean of all the No. 12 hard-drawn wires and subtracting, the result is 2.57%. This value agrees with the above, within the mean deviation above. The value may, therefore, be stated to be 2.7%

For the No. 18 wires the mean difference was 3.09%.

2. COPPER OF ESPECIALLY HIGH CONDUCTIVITY

Samples of electrolytic copper wire, drawn directly from cathode plates without intermediate melting, were prepared for this investigation by two of the refiners, the U. S. Metals Refining Company and the Baltimore Copper Smelting and Rolling Company. The values of resistivity and conductivity for two samples from each refiner are given herewith. The first three samples were annealed, and the fourth was a hard-drawn No. 12 wire.

Ohms per meter-gram at 20° C	Percent conductivity
0.15101	101.33%
0.15098	101.35%
0.15076	101.50%
0.15386	99.46%

It was thought that still higher conductivity could be obtained by melting the cathode plates in vacuo, and drawing wires from the rods resulting. This was carried out, with the assistance of

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the Research Laboratory of the General Electric Company, and Mr. W. H. Bassett, of the American Brass Company. The results on a sample melted in a hole of 2 cm diameter in a special crucible of Acheson graphite are given herewith. The first is for annealed wire, and the second for hard-drawn No. 18 wire:

Ohms per meter-gram at 20° C	Percent conductivity
0.15046	101.70%
0.15483	98.83%

Other samples melted in alumina and graphite crucibles had conductivity less than before the vacuum treatment. It is believed that better results in this direction could be obtained, but time to attack the problem was not available.

Wires were submitted by the Quincy Mining Company, drawn from a mass of native lake copper of unusually high conductivity. The copper had never been melted down. The values found are given herewith. The first is a hard-drawn No. 12 wire, the second annealed.

Ohms per meter-gram at 20° C	Percent conductivity
0.15431	99.17%
0.15045	101.71%

3. DATA ON HARD-DRAWN ALUMINUM

Seven samples of wire, together with the following table of information, were furnished by the Aluminum Company of America.

TABLE III

Sample No.	Conductivity	Analysis		
		Al	Si	Fe
1	62.1	99.58	.27	.15
2	61.6	99.60	.26	.14
3	61.6	99.58	.27	.15
4	61.6	99.59	.27	.14
5	61.8	99.59	.27	.14
6	62.0	99.55	.31	.14
7		99.52	.34	.14

The results of measurements at the Bureau of Standards are given in the following table:

TABLE IV

Sample No.	Size of wire B. and S.	Density	Ohms per meter-gram at 20.00° C	Micro-ohms per cm cube at 20.00° C	Percent conductivity on meter-gram basis	Percent conductivity on cm cube basis
1	6	2.6983	0.07575	2.8074	202.01%	61.31%
2	6	2.6996	0.07604	2.8168	201.23%	61.11%
3	6	2.6994	0.07579	2.8076	201.91%	61.31%
4	6	2.6992	0.07602	2.8165	201.30%	61.11%
5	6	2.6992	0.07605	2.8175	201.21%	61.09%
6	12	2.6991	0.07535	2.7917	203.08%	61.66%
7	16	2.6984	0.07514	2.7845	203.66%	61.82%
Mean		2.6990	0.07573	2.8060	202.06%	61.34%

The two values assumed as standard in computing the two percent conductivities are the values assumed in the case of copper, viz, 0.153022 ohm per meter-gram at 20° C, and 1.72128 micro-ohms per cm cube at 20° C.

The company also furnished a figure representing the mean conductivity of its output of all sizes of wire for the past five years. The figure was obtained by averaging the records for one out of every 15 conductivity tests during the above period. As the figure is the result of many thousands of separate determinations it is of great value. This figure was given as "61.38 on the Matthiessen standard scale." This was translated into resistivity values by applying as a correction the difference between the mean of the percent conductivity values on the first six samples above, as determined by the company, and as determined at the Bureau of Standards, and using the mean density found above. The correction takes into account both errors of measurement and a difference in the standard values assumed.

The results then were:

Percent conductivity on cm cube basis = 60.86%
Resistivity in micro-ohms per centimeter cube at 20° C = 2.8283
Resistivity in ohms per meter-gram at 20° C = 0.07633
Percent conductivity on meter-gram basis = 200.46%

IV. DISCUSSION OF RESULTS

1. ANNEALED COPPER WIRES

(A) SUMMARY OF ABOVE DATA

It was found that annealed copper wires did not differ in conductivity with the size of wire. For the annealed samples from 14 important producers the mean results were:

Resistivity in ohms per meter-gram at 20° C = 0.15292
Percent conductivity = 100.07%

The average deviation from these means was 0.26 percent, and the maximum deviation of any group was 0.81 percent. The general agreement of the results indicates that the refiners are producing copper very satisfactory in its uniformity of quality.

(B) SUMMARY OF DATA FROM AMERICAN BRASS COMPANY

We present here also the results of the data collected by the American Brass Company, which were furnished by Mr. W. H. Bassett, and which are given with his permission. Measurements were made upon annealed No. 12 samples, at least one sample from each carload of wire bars. The wire bars represented a number of the important refiners of copper. Practically all the material had been electrolytically refined. For samples from more than 2000 carloads, or more than 100 000 000 pounds of wire bar copper:

Mean resistivity in ohms per meter-gram at 20° C = 0.15263
Mean percent conductivity = 100.25%

This result is regarded as reliable, as the work of this laboratory is known to be done with care, and as its standards for conductivity measurements are in agreement with those of the Bureau of Standards. This result is much more representative, in pounds of copper, than the result just given above. The fact that the value for conductivity is higher is corroborative of the former result, because this company (like others who make conductivity tests) accepts only copper of the higher conductivity.

It is to be observed that both the mean values as found in this investigation, and as found by Mr. Bassett, for the resistivity and percent conductivity differ from the standard values (0.153022 and 100 percent) by less than 0.26 percent, which is the above average deviation from the mean. It is interesting that the standard values, derived from the experiments of fifty years ago on copper supposed to be chemically pure, are so close to the average of commercial copper to-day. It at once suggests itself that the present standard of resistivity is a good one to retain for commercial copper.

2. HARD-DRAWN COPPER WIRES

The results on the hard-drawn wires may best be summarized by considering the difference in conductivity between annealed and hard-drawn samples. It was found that this difference in conductivity varies with the size of the wire. Most of the wires used were No. 12 B. and S., and for that size *the conductivity of annealed wires was found to be greater than the conductivity of hard-drawn wires by 2.7 per cent.*

Only a few No. 6 and No. 18 wires were experimented upon, and the mean results are stated above. The values are not considered as having much weight, being based on such limited experimental evidence, but they show, as was to be expected, that the difference between the conductivity of annealed and hard-drawn wires increases as the diameter of the wire decreases. This general conclusion is, however, complicated in any particular case by the particular practice of the wire drawer, in regard to the number of drawings between annealings, amount of reduction to each drawing, etc.

3. THE HIGHEST CONDUCTIVITY FOUND

The lowest resistivity and highest conductivity found, for a *hard-drawn* wire, were:

Resistivity in ohms per meter-gram at 20° C = 0.15386
Percent conductivity = 99.46%

and for an *annealed* wire, were:

Resistivity in ohms per meter-gram at 20° C = 0.15045
Percent conductivity = 101.71%

The former wire was drawn from a cathode plate without melting. The latter wire was drawn directly from a mass of native lake copper which had never been melted down. It was thought that a still higher conductivity could be obtained if a wire could be prepared from cathode copper which had been melted in vacuo. This was tried and no material increase of conductivity was obtained. This may, however, have been due to contamination from the crucibles or to the poor mechanical condition of the samples resulting from the melting. It is believed that further investigation along this line, with care in the methods of cooling, might be rewarded with a higher conductivity than any yet obtained.

4. ALUMINUM

Data on the conductivity of hard-drawn aluminum is given above. For 7 samples of commercial aluminum, supposed to be fairly representative of the present output of the Aluminum Company of America, the mean results were:

Resistivity in ohms per meter-gram at 20° C = 0.07573
Resistivity in micro-ohms per centimeter cube at 20° C = 2.8060
Density = 2.699

The chemical analysis of these wires is also given above. The mean resistivity of the company's output of all sizes of wire for the past five years was furnished by the company. The value was given by the company in terms of the resistance per centimeter cube, and has been reduced to the meter-gram basis by the use of the density just stated. The values are:

Resistivity in ohms per meter-gram at 20° C = 0.07633
Resistivity in micro-ohms per cm cube at 20° C = 2.8283
Percent conductivity on cm cube basis = 60.86 %
Percent conductivity on meter-gram basis = 200.46 %

This result is considered to be a very good average value for commercial hard-drawn aluminum. It is, of course, entitled to much greater consideration than the above results on 7 samples.

Aluminum wire is always furnished hard-drawn, hence no data is given on annealed samples.

5. TEMPERATURE COEFFICIENT OF COPPER

The work on the temperature coefficient, reported in the paper on "The Temperature Coefficient of Resistance of Copper,"[8] was done upon samples included in this investigation. The temperature coefficient was found to be linear between 10° C and 100° C to an accuracy within 0.2 %, and to be proportional to the conductivity, the mean deviation from this relation being only 0.2 % for the 37 samples measured. The temperature coefficient at 20° C of a sample of copper is accordingly given by multiplying the number expressing the percent conductivity decimally by

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[8] This Bulletin, 7, p. 71; 1910.

$$0.00394$$

In the paper mentioned is given a table showing the temperature coefficients for various conductivities over the range of commercial copper, calculated according to the above simple rule. The relation between conductivity and temperature coefficient may be expressed otherwise, thus: the change of resistivity per degree C is a constant for copper, independent of the temperature of reference and independent of the sample of copper. This constant is:

0.000598 ohm per meter-gram,
or, 0.00681 micro-ohm per centimeter cube.

Cases sometimes arise in practice where a temperature coefficient of resistance must be assumed. It may be concluded from these results that the best value to assume for the temperature coefficient of good commercial *annealed* copper wire is that corresponding to 100 % conductivity, viz:

$$\alpha_0 = 0.00428, \quad \alpha_{15} = 0.00402, \quad \alpha_{20} = 0.00394, \quad \alpha_{25} = 0.00386$$

$\left(\alpha_{20} = \dfrac{R_t - R_{20}}{R_{20}(t-20)}, \text{ etc.}\right)$. This value would usually apply to instruments and machines, since they are generally wound with annealed wire. Similarly, the temperature coefficient of good commercial *hard-drawn* copper wire may be taken as that corresponding to a conductivity 2.7 % less, viz:

$$\alpha_0 = 0.00415, \quad \alpha_{15} = 0.00391, \quad \alpha_{20} = 0.00383, \quad \alpha_{25} = 0.00376.$$

V. CONCLUSIONS

1. BEST VALUE FOR THE RESISTIVITY OF ANNEALED COPPER

The mean value found for the 20° C resistivity of commercial annealed copper is very close to the standard value previously assumed by the Bureau of Standards and by the American Institute of Electrical Engineers before 1908. We are accordingly led to the conclusion that the best value to be assumed for the resistivity of annealed copper, in the preparation of wire tables and in the expression of percent conductivity, etc., is said standard value, viz:

0.153022 ohm per meter-gram at 20° C

Thus, three of the standard 20° C values in Table I, page 105, are in agreement. The standard values at other temperatures, however, are not in agreement because of differences in the temperature coefficient assumed. Applying the temperature coefficient which is discussed above, page 120, and which is equivalent to a change of resistivity per degree C

$$= 0.000598 \text{ ohm per meter-gram,}$$

we obtain the following values of the standard resistivity at various temperatures:

Temperature Centigrade	Resistivity in ohms per meter-gram
0°	0.1411
15°	0.1500
20°	0.153022
25°	0.1560

It will be noticed that the value 0.1500 at 15° C is a round number easily remembered, and happens to agree with the 15° C value of the Matthiessen Standard as computed by Lindeck (col. 4, Table I). It is proposed that the resistivity represented by the foregoing values be called the "**Annealed Copper Standard.**" (The term "Matthiessen Standard" has been applied to too many different values to be considered.)

2. DENSITY OF COPPER

When it is desired to calculate the resistance of wires from dimensions, it is necessary that a density be given, as well as the meter-gram resistivity. *It is proposed that the standard density for copper, at 20° C, be taken as 8.89.* This is the value which has been used by the A. I. E. E., and most other authorities. Measurements made on a number of the samples in this investigation indicated this value as a mean. This density, of 8.89, at 20° C, corresponds to a density of 8.90 at 0° C. Applying the above values of density and of meter-gram resistivity, the resistivity of the "Annealed Copper Standard" is found to be equivalent to a specific resistance of 1.72128 micro-ohms per centimeter cube at 20° C, or a specific conductivity of $5.8096\ (10)^{-4}$ cgs units at 20° C.

3. TEMPERATURE COEFFICIENT OF ANNEALED AND OF HARD-DRAWN COPPER

According to the above discussion of the temperature coefficient, page 120, it is proposed that, in cases where assumption is unavoidable, the temperature coefficient of good commercial *annealed* copper wire be assumed as:

$$\alpha_0=0.00428,\quad \alpha_{15}=0.00402,\quad \alpha_{20}=0.00394,\quad \alpha_{25}=0.00386,$$

and that the temperature coefficient of good commercial *hard-drawn* copper wire be assumed as:

$$\alpha_0=0.00415,\quad \alpha_{15}=0.00391,\quad \alpha_{20}=0.00383,\quad \alpha_{25}=0.00376.$$

4. PERCENT CONDUCTIVITY

Percent conductivity of a sample of copper may be calculated by dividing the resistivity of the Annealed Copper Standard at 20° C by the resistivity of the sample at 20° C. Inasmuch as the temperature coefficient of copper varies with the conductivity, it is to be noted that a different value will be found if the resistivity at some other temperature is used. This difference is of practical moment in some cases. For example, suppose the resistivity of a sample of copper is 0.1594 at 20° C; dividing 0.1530 by this, the percent conductivity is 96.0%. Now the corresponding 0° C resistivity of the sample is 0.1474; dividing 0.1411 by this, the percent conductivity is calculated to be 95.7%. In order that such differences shall not arise, it is suggested that the 20° C value of resistivity always be used in computing the percent conductivity of copper. When the resistivity of the sample is known at some other temperature, *t*, it is very simply reduced to 20° C by adding the quantity, (20-*t*) multiplied by 0.000598 ohm per meter-gram.

5. DATA FOR USE IN WIRE TABLES

The data available from this investigation for use in connection with the preparation of wire tables are, in addition to the foregoing values for (1) the resistivity and (2) the temperature coefficient of copper, the following: (3) the difference, 2.7%, between the conductivity of annealed and hard-drawn No. 12 copper wire, together with a recognition of the general increase of this difference as the diameter of the wire decreases; (4) data on commercial hard-drawn aluminum, as follows:

ALUMINUM

Resistivity in ohms per meter-gram at 20° C	=0.0763
Micro-ohms per cm cube at 20° C	=2.828
Density	=2.70

6. THE EXPRESSION OF RESISTIVITY IN OHMS PER METER-GRAM

The advantages of the expression of resistivity in terms of ohms per meter-gram may well be emphasized here. In specifications for purchase, or in expressing the results of conductivity measurements, the statement of the meter-gram resistivity avoids all questions of standard values which arise in connection with the percent conductivity. The use of the meter-gram basis corresponds most closely to the usual methods of making conductivity measurements in practice. There are cases, however, in which the cross-section is measured and not the mass, and hence the centimeter cube resistivity obtained. The difficulty of expression in terms of percent conductivity at once arises, that percent conductivity can be computed either from the meter-gram resistivity or the centimeter cube resistivity. If the density of the sample differs from the standard density, these two percent conductivities will not agree. This difficulty is made particularly clear by an inspection of the data on aluminum given above, page 121.

The extreme difference between the percent conductivities on the two bases makes manifest the absurdity of the extension of the idea of percent conductivity to metals of different density from that of copper, *unless* it be stated upon which basis the percent conductivity is reckoned. Thus, we may speak of the "percent conductivity on the meter-gram basis," and the "percent conductivity on the centimeter cube" basis. It is suggested that these terms be shortened, respectively, to the "mass percent conductivity" and the "volume percent conductivity," which terms should be readily understood. The various sources of possible confusion in the use of percent conductivity make it desirable that the actual restivity be stated. The meter-gram resistivity is preferable to the centimeter cube resistivity, because (1) *the measurement of cross section in many cases is difficult and inaccurate;* (2) *the direct measurement of cross section is practically impossible for irregular shapes of cross section;* (3) *copper is sold by weight rather than by volume, and therefore the data of value to most users is given directly by the meter-gram resistivity.*

7. DESIRABILITY OF AN INTERNATIONAL STANDARD OF COPPER CONDUCTIVITY

It is desired that the foregoing data and suggestions shall not confuse existing practice, and it is not expected that they will make any change in the electrical engineering practice of this country until taken cognizance of by the American Institute of Electrical Engineers. Furthermore, an international agreement on copper standards is considered desirable. To ascertain whether this might be possible, the Bureau of Standards has had some preliminary correspondence with the national laboratories of Germany, England, France and Austria. Considerable interest was manifested in the matter. The use of the meter-gram basis was looked on with favor. In Germany and England the matter was referred to the national electrical engineering societies. No definite consideration has been as yet given by these bodies to the matter of international copper standards. Particularly in view of the fact that the vast bulk of the world's copper is mined and refined in the United States, it would seem appropriate for the American Institute of Electrical Engineers, through the International Electrotechnical Commission, to lead an attempt to secure agreement among the various engineering bodies. It is desired that none of the proposals in this paper should stand in the way of such an international agreement. It might seem desirable to base the international standard resistivity upon the purest copper that can be produced, instead of upon such an average of the commercial product as is given in this paper. However, difficulties arise in that direction. Finally, it is believed that the expression of conductivity on a percentage basis will be thoroughly satisfactory only after a definite international standard has been established.

VI. SUMMARY

1. The various standard values in use for the resistivity and temperature coefficient of copper are given, and the need for the present investigation shown.

2. The means of making precise measurements of conductivity of wire samples is described.

3. The resistivities are given for 89 samples of commercial copper from 14 important refiners and wire manufacturers in this and other countries. The mean for annealed wires is:

Resistivity in ohms per meter-gram at 20° C = 0.15292
Percent conductivity = 100.07%

(Percent conductivity is computed on the basis of 100% conductivity corresponding to the standard resistivity, 0.153022 ohm per meter-gram at 20° C.) The mean result of data furnished by a large wire manufacturing company, representing tests on more than 100 000 000 pounds of copper, is also given, viz, for annealed samples:

Resistivity in ohms per meter-gram at 20° C = 0.15263
Percent conductivity = 100.25%

It is concluded that the best value to be assumed for the resistivity of *annealed* copper, in the preparation of wire tables and in the expression of percent conductivity, etc., is the previously used standard value, viz:

0.153022 ohm per meter-gram at 20° C.

4. The conductivity of hard-drawn No. 12 B. and S. wires was found to be less than the conductivity of annealed wires by a mean value of 2.7%. The difference between the conductivity

of annealed and hard-drawn wires increases as the diameter of the wire decreases.

5. The lowest resistivity and highest conductivity found, for a *hard-drawn* wire, were:

Resistivity in ohms per meter-gram at 20° C = 0.15386
Percent conductivity = 99.46%

and for an *annealed* wire, were:

Resistivity in ohms per meter-gram at 20° C = 0.15045
Percent conductivity = 101.71%

6. Representative mean values for commercial hard-drawn aluminum were obtained, as follows:

Resistivity in ohms per meter-gram at 20° C = 0.0763
Resistivity in micro-ohms per cm cube at 20° C = 2.828
Density = 2.70

7. The work on the temperature coefficient of resistance of copper, which is reported in another paper,[6] was done upon samples included in this investigation. The temperature coefficient was found to be substantially proportional to the conductivity. This relation may be expressed thus: the change of *resistivity* per degree C is a constant for copper, independent of the temperature of reference and independent of the sample of copper; this constant is

0.000598 ohm per meter-gram.

8. The advantages of the expression of resistivity in ohms per meter-gram are stated.

9. The desirability of an international standard of copper conductivity is urged.

WASHINGTON, August 1, 1910.

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[6] This Bulletin, 7, page 69; 1910.

ON THE CONSTANCY OF THE SULPHUR BOILING POINT

By C. W. Waidner and G. K. Burgess

In view of the general use and convenience of the sulphur boiling point as a temperature for the standardization of thermometric apparatus, it is highly desirable to demonstrate conclusively by experiment that we are really dealing with a strictly reproducible and satisfactorily constant temperature throughout the column of vapor in the standard form of sulphur boiling apparatus, which is generally used.

We have recently shown[1] that in the ordinary form of Callendar and Griffiths apparatus, in which the sulphur is boiled in a glass tube some 45 cm long by 4.5 cm diameter, heated from below either electrically or by a gas burner, and in which the thermometer coil, mounted within a porcelain tube glazed on the outside, is inclosed in a cylindrical or conical radiation shield of aluminum of some 15 cm in length; the temperature of the sulphur vapor, as measured with resistance thermometers having coils 4 to 5 cm long, is apparently constant to within 0°.03 C throughout some 27 cm of the 30 cm length of the column of sulphur vapor.

With thermocouples of platinum-rhodium and of platinum-iridium, however, discordant results were obtained, varying both with the couple and depth of immersion of the wires in the vapor and indicating an apparent point-to-point variation within the radiation shield of the order of 0°.5 C.

Since it might be maintained that the relatively long resistance thermometer is an integrating device giving an average temperature within the shield whose real temperature would be far from constant as shown by the thermocouples which presumably give the temperature at a point, we have thought it worth while to endeavor to remove any existing doubts as to the constancy of the temperature of sulphur vapor in this apparatus by further experiments.

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[1] This Bulletin 6, pp. 149-230; 1910.

It should first be noted, perhaps, that the resistance thermometer, if it can be made small enough, is more suited than the thermocouple for the measurement of small differences in temperature at the sulphur point, as the indications of the former, read as a strictly potential instrument, may be freed from any thermoelectric phenomena occurring in the lead wires; whereas in the case of the latter, such effects are additive, and when they occur in the platinum or alloy leads can not be distinguished from the E. M. F. of the junction.

We have therefore used, for the exploration of the temperature in the sulphur apparatus, in addition to several thermocouples, a resistance thermometer of very short coil, less than 9 mm in length. Its resistance at the S. B. P. was about 13.1 ohms, the measuring current 0.006 amperes, causing a rise of less than 0°.01 C. in the temperature of the thermometer coil. The potential terminal method of measurement was used (see above reference), permitting changes of less than 0°.02 C. to be detected with certainty.

Using either the cylindrical or conical radiation shield, with umbrella top to eliminate condensation cooling, and taking measurements at various depths of immersion in the vapor, and for all positions within the shields up to 2 cm of the top, no variations as great as 0°.05 C were observed. In the following table, for example, are given the results on two series of measurements for the distribution within the cylindrical shield, the zero position being at the lowest position in the shield corresponding to the bottom of the long resistance thermometers previously used.

Depth of Immersion of Shield in S Vapor	**0**	**5**	**10**	**Distance Thermometer raised in cm**
25 cm	**13.128**	**13.127**	**13.128$_5$**	**Resistance of Therm.**
28 cm	**13.126**	**13.126**	**13.127**	**Resistance of Therm.**

Outside the radiation shield, of course, the temperature falls off rapidly due to the cooling effect of the liquid running down the tube and to radiation.

Various thermocouples of wire 0.6 mm diameter and which had been subjected to high temperature usage were tried, with results varying from 0°.0 to 1°.0 for the apparent range of temperature within the shield. Even with a differential thermocouple, a distribution differing by several tenths degree was obtained according as one junction or the other was raised. The most uniform distribution was found with couples which had been used the least at high temperatures. Finally, in order to eliminate the effects both of conductivity and of heterogeneity in the wires, we used a couple of which the wires were 0.1 mm diameter and which had been annealed and calibrated once, but not otherwise used. With this very fine and electrically homogeneous thermocouple, most satisfactory results were obtained for the temperature distribution in the shield as shown below for an immersion of 27 cm.

Distance couple raised in cm	2	4	6	5	7	9	11	3	6	9	5	etc.
Change in temperature °C	+.03	0	0	+.01	+.01	−.03	+.04	+.06	+.02	−.04	+.02	etc.

These variations are of the order of the error of measurement and of barometric fluctuations.

It appears to be proved, therefore, by a point to point exploration within the radiation shield of the standard form of S. B. P. apparatus by means of suitable resistance and thermoelectric thermometers and for any position of the shield throughout nearly the whole length of the sulphur vapor column, that the temperature is certainly constant to within 0°.05 and probably within 0°.03 C.

As shown previously,[2] the most probable numerical value of the S. B. P. on the scale of the constant volume nitrogen thermometer, as deduced from all the available data, is 444.7_0 to within 0°.1 C, with a variation of about 0°.09 per mm Hg change in pressure.

In spite of the complexity of sulphur in its chemical behavior, such as possessing several valences and isomeric forms in the solid and liquid states, the fixity of the temperature of its vapor during boiling appears to be all that could be desired. It would seem that the only phenomenon that could cause this constancy to be questioned would be the existence of two forms of liquid sulphur of slightly different boiling points and one form gradually changing into the other with continued boiling. We have never been able to detect any such progressive change in the boiling point over several hours' time. A further test of the constancy of this temperature is the remarkably close agreement on extrapolation to such high temperatures as the silver and copper points (loc. cit.), using for calibration, sulphur that had been reboiled many and few times.

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[2] Waidner and Burgess, Bulletin Bureau of Standards, 7, pp. 3–11; 1910.

We may therefore say with a considerable degree of positiveness that the temperature defined by the S. B. P. apparatus may readily be reproduced to within 0°.05 with reasonable care; and as compared with the fixed points, either temperatures of freezing or boiling, given by any of the chemical elements, the S. B. P. is the one the most exactly defined, the most certainly reproducible, and the most constant yet studied.

WASHINGTON, December 6, 1910.

NOTE ON OSCILLATORY INTERFERENCE BANDS AND SOME PRACTICAL APPLICATIONS

By George O. Squier and Albert C. Crehore

In making measurements of any kind the observer usually requires that some form of mass shall be moved. The agencies employed to move this mass afford a convenient means of classifying instruments into four general groups according as the forces are applied:

I. Mechanically.
II. By Heat.
III. By the Magnetic Field.
IV. By the Electric Field.

These groups may be subdivided by taking account of the manner in which the matter to be moved is observed. The present inquiry chiefly concerns one method of noting this in an indirect way by observing the motion of interference bands or fringes. By this means the motion of the matter is derived and may be measured accurately if desired.

The marvelous beauty, sensibility, and accuracy of light interference phenomena are well known, but they are only fully appreciated by those very few specialists who devote their attention to these subjects. Such considerations have led the authors to devise some new types of instruments which are simple in construction, portable, and yet attain a sensibility at present only reached by laboratory apparatus. Instruments illustrative of each of the four classes above mentioned have been constructed.

Interference phenomena in light are many and varied in character, the principal examples being those produced by thin plates, including Newton's rings, thick plates, reflection by mirrors, diffraction, and that produced by two similar point sources, together with additional phenomena due to polarization. The instruments to be described make use of interference by thin plates and reflection by mirrors and opportunity has not been presented to examine other methods of interference applied to similar purposes.

OSCILLATORY BANDS

If a plate of glass is laid upon a second plate, which may be glass or any substance having a surface that will reflect light, it is well known that brilliant bands, being alternately light and dark in character, may be seen by reflection if the source of light is monochromatic. The geometrical character of the surfaces can be determined by observing the contour of the curves followed by these bands. Ordinary pieces of window glass produce these bands very well, but they are curved in various ways indicating that the surfaces are not plane. If the surfaces are optically plane, and the upper plate rests by its own weight upon the lower plate, the bands are usually formed in straight lines. The more nearly parallel to each other the planes become, the greater the distance between the bands. The two planes form a wedge with a very small acute angle, and the edge of this wedge, where the planes intersect, is a line parallel to the bands.

A pressure applied to some point of the upper plate, so as to press the two plates nearer together, produces two separate effects. It alters not only the angle of the wedge, but also rotates the edge through a considerable angle. These changes affect the bands each in its own way, the first broadening them and increasing the distance between adjacent bands; the second rotating the whole parallel system of bands by the same angle by which the edge of the wedge is rotated.

With large plates the air imprisoned between them retards any rapid motion of readjustment after a pressure is applied, but with plates of smaller area and mass, from 5 to 10 millimeters in diameter, there is a quick response to a change of pressure, and the angular motion of the bands is proportionally greater for a given change. In using such plates in the instruments to be described the pressure between them is varied, and a consequent motion of the bands produced, an alternating force causing an oscillatory motion of the bands. The types of instruments therefore differ according to the means for varying the pressure.

I. PRESSURE MECHANICALLY APPLIED

Fig. 1 shows an instrument for detecting or measuring small changes of pressure. A diaphragm, D, is clamped between the solid metal pieces, A and B, in such manner as to enclose a small air chamber, C, provided with an outlet, T. At the center of the disc is cemented a piece of plane optical glass, P_1, and upon this a similar plate, P_2, is laid, merely resting by its own weight. An observer looks into the instrument from above and sees the light from some convenient monochromatic source reflected from the two glass plates. The interference bands appear clear and distinct and are straight.

Any change of pressure of the air within the chamber, C, the atmospheric pressure without remaining constant, deflects the diaphragm and carries both plates together, either up or down, according to circumstances, but this alone will not change permanently the pressure between the glass plates, which is necessary to move the bands. If the upper plate were held stationary with respect to the frame, A B, while the lower plate moved, this would move the bands. The object may be accomplished in a very simple manner by the use of a rigid steel rod or "pointer" attached to the frame and adjustable until it makes contact with the upper glass plate.

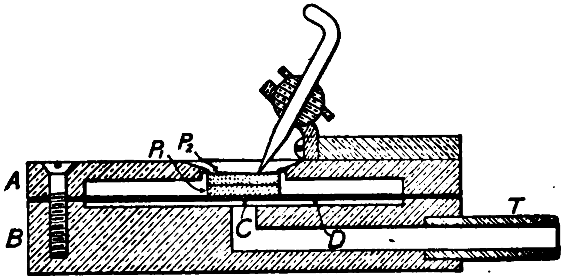

Fig. 1. *Section of Interference Instrument for Varying the Pressure Mechanically. Designed for Physiological Measurements*

In adjusting this pointer the bands change to a new position at the first contact and remain as long as the pressure is the same. For a given setting of the pointer an increase of pressure in the chamber moves the diaphragm outward and increases the pressure between the glass plates. The use of a pointer localizes the pressure at one point of the upper plate and produces the changes above described. The bands broaden out, and their direction revolves through an angle dependent upon the amount of increase of pressure. If the air pressure is made to increase and decrease, the system of bands oscillates in phase with the pressure changes.

The pointer is so constructed in a ball and socket joint, the ball being split so that the pointer slides friction-tight through it, that it can be moved easily to any part of the surface of the upper glass plate, for it is found that there are critical points on the plate where the sensibility of the instrument is greatly increased. In exploring the plate with the pointer for an initial setting it has been found that particular areas are much more senstitive to minute changes in pressure than the remainder of the plate. It is easy to obtain an angular motion of 180 degrees for small changes in the adjustment of the pointer.

With this instrument a sufficient change of pressure of the air is obtained to oscillate the bands through a large angle by connecting it to the pulse at the wrist with an ordinary stethoscope and rubber tube as shown in Fig. 2. In this manner the character of the human heart action has been observed visually by the movement of the bands.

Fig. 3 shows two photographic cardiograms taken by means of the instrument shown in Fig. 1. In addition, an ordinary camera having a plate holder adapted to move the plate past a slit and a plane glass mirror to turn the light reflected from the interference plates horizontally into the camera were used. A very convenient source of light is an ordinary commercial mercury-vapor lamp. It does not give pure monochromatic light, but the bands are very distinct, the predominant colors being violet and green. For photographic purposes it is very superior, and any rapid photographic plate gives good results.

II. PRESSURE PRODUCED BY HEAT

In the diagram Fig. 4 two plates of ordinary glass, ABCD and EFGH, were used, the lower plate being first silvered over its whole surface and a portion, AJB and CKD, removed. The silver remaining includes the narrow neck JK between the terminals L and M. The upper plate is secured by clamps so as to cover this neck, leaving an area for observing the interference bands between the plates. Bands appear throughout the entire extent of the upper plate, but are less brilliant over the silver. Upon passing

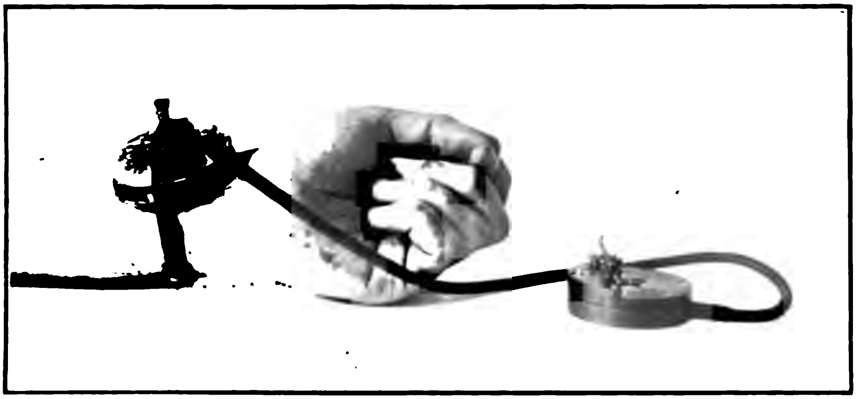

Fig. 2. *Method of Connecting Instrument for Observing Heart Action*

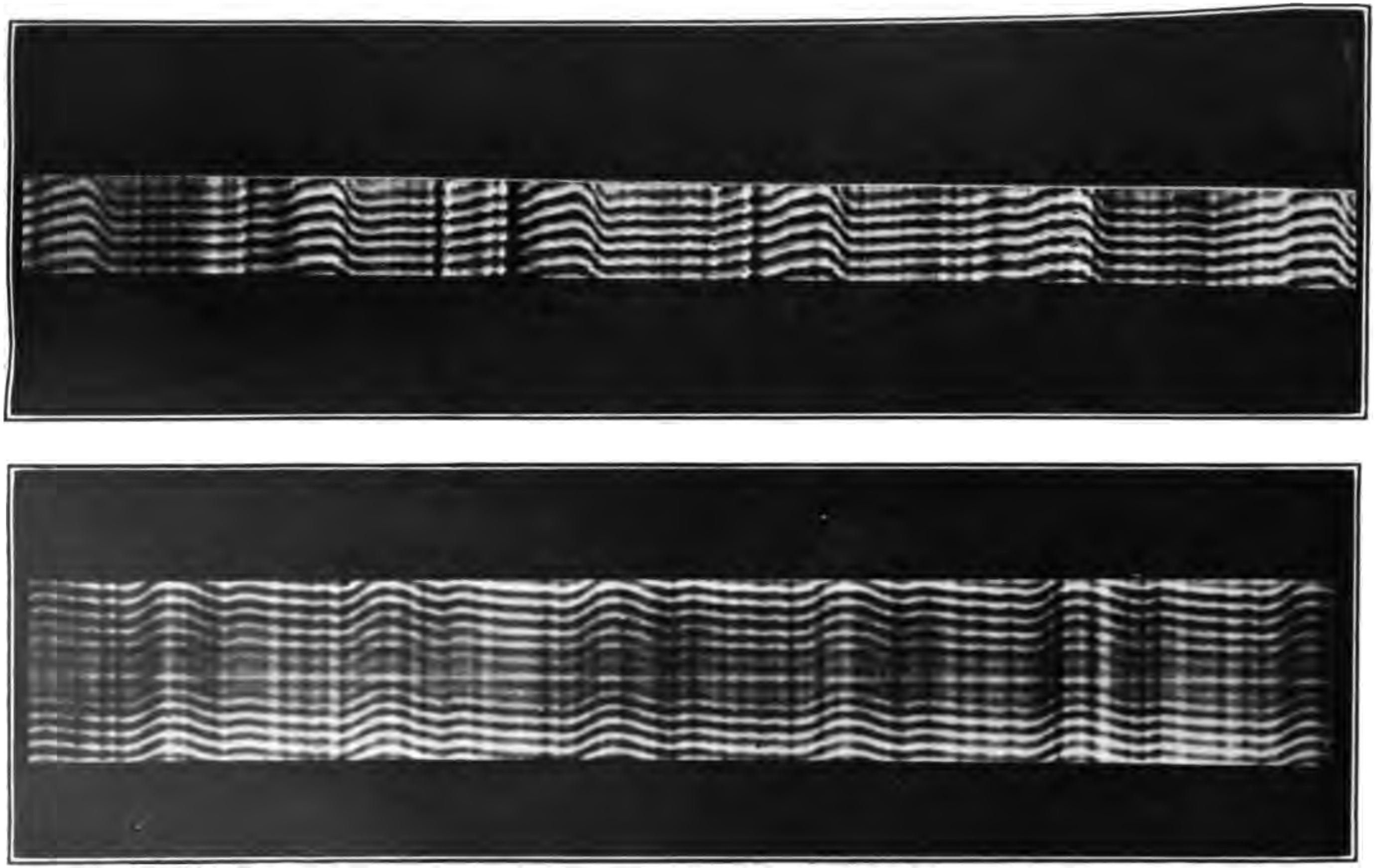

Fig. 3. *Human Cardiograms taken with Instrument of Fig. 1, Showing Five Complete Periods. Two Different Male Subjects*

Upper curves read from right to left; lower curves from left to right

an electric current the heat developed is localized in the narrow neck at the center of the plates. At this point the glass of both plates expands, making a small elevation on each plate, forcing them apart and shifting the interference bands. In a first attempt at an instrument of this kind, with a resistance between terminals of 51 ohms, it required as much as 0.18 watts to cause an observable motion of the bands. Current 0.063 amperes and volts 2.9. Other instruments of similar construction were made having different resistances at the neck. With a resistance of 1,800 ohms, 0.16 watts were required to move the bands approximately the same as above. Current, 9 milliamperes.

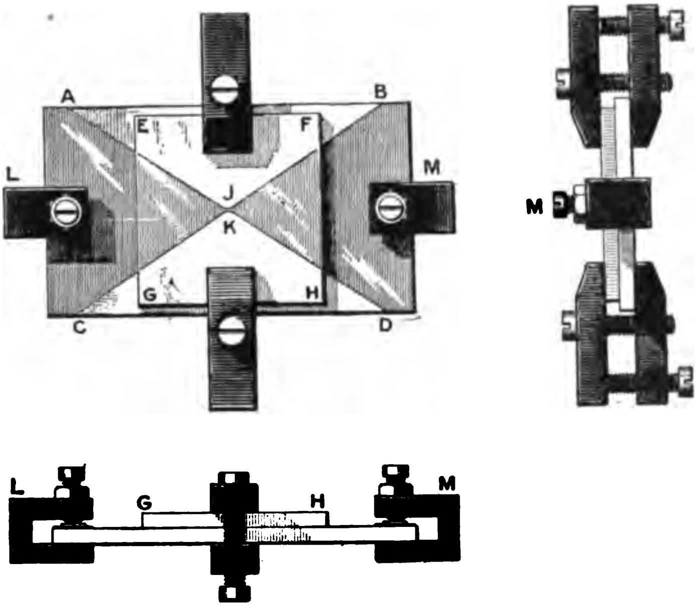

Fig. 4. *Interference Instrument Operated by Heat. Silver Between Two Plates of Glass*

Approximately the same number of watts is required to move the bands with widely different resistances. It thus appears that this amount of heat is a quantity imposed by the nature of silver and glass. The sensibility is limited by their coefficients of expansion. Hard rubber was tried as being a substance of large coefficient of expansion, but since it is opaque, the bands were observed from the opposite side of the silvered plate. They can only be seen over those portions of the glass where the silver is absent, and are not so brilliant with rubber as with glass, but yet sufficiently distinct to be used. The coefficient of expansion of hard rubber is 7 or 8 times that of glass. A motion of the bands was produced with 0.005 watts, current 10 milliamperes, and resistance 50 ohms. Substituting gutta-percha for hard rubber increased the sensibility to 0.0014 watts.

Another form of heat instrument, Fig. 5, represents a glass plate silvered on the upper surface and provided with terminals as in Fig. 4. A piece of mica, as nearly plane as possible, 0.0075 mm thick and 1 cm square is pressed against the glass so as to cover the neck. In this condition the mica adheres to the glass so that it is not easily displaced. The bands are brilliant, having various curved contours. With such plates there generally occur two kinds of critical points, one elliptical and the other hyperbolic in character. The points of contact are at the centers of elliptical areas, and the points of greatest separation are at the centers of two sets of curves hyperbolic in character. Any motion is most apparent at these points, and the sensibility is increased by moving the mica plate over the neck so as to bring one of these critical points into its neighborhood.

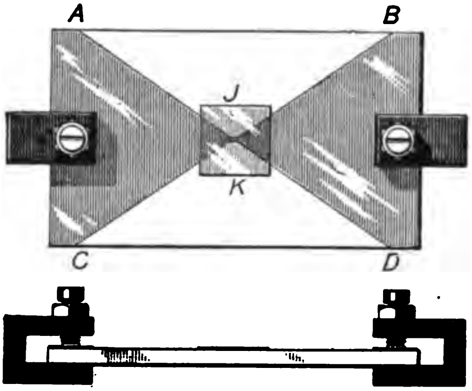

Fig. 5. *Interference Instrument Operated by Heat. Silver Between Glass and Thin Mica Plates*

When the neck was cut across with a knife edge and powdered graphite substituted, the sensibility was as follows:

Resistance	129 ohms.
Current	0.00093 amperes.
EMF	0.12 volts.
Power	0.000113 watts.

This increase in sensibility is due to the small mass of the mica plate which rested without clamps by its own weight upon the glass. The mica being easily flexed and not plane exhibits individual peculiarities. The time required for the bands to assume their final position is so brief that Morse signals may be read at a rapid rate in any of the forms of heat instruments described.

III. PRESSURE VARIED BY THE MAGNETIC FIELD

The optical apparatus for producing oscillatory bands is readily made operative by the magnetic field. A convenient method is to mount the glass plates upon an iron diaphragm acted upon by a magnetic field as in a telephone receiver.[1] The order of magnitude of the sensibility obtained by using a telephone receiver in this manner is:

Resistance	620 ohms.
Current	1.26×10^{-6} amperes.
EMF	0.00077 volts.
Power	9.8×10^{-10} watts.

A telephone used optically in this way is applicable to wireless telegraphy. Wireless messages have been received by merely removing the telephone now commonly used, and substituting the optical telephone in its place, without making any change whatever in the arrangement of the electrical circuits. Both the optical receiver and the telephone receiver have been used simultaneously by the same person, the two instruments being connected in circuit at the same time. This permits an observer to both see and hear a wireless message simultaneously. The probable advantages of two physiological senses to examine corroboratively and simultaneously a single phenomenon are worthy of careful investigation.

When no signal is being sent from the transmitting station, the bands remain at rest in a given fixed position. When a signal is received the bands rotate quickly to a new position depending upon the energy of the received signal and remain in the new position until the termination of the signal. Dots and dashes are thus easily read.

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[1] Barus.: Am. J. Sci. (4) **3**, 219; 1897.

In adapting a telephone to vary the pressure by the magnetic field, it should be remembered that it is designed primarily for the ear, whereas what is here desired is maximum displacement for a minimum of applied energy. A marked increase of sensitiveness has been obtained by nothing more than a redistribution of the iron in the diaphragm. The ultimate sensibility of this galvanometer will only become known when its electro-magnetic system has received the same careful design as is now given to other galvanometers for special purposes.

It is frequently desirable to make measurements of alternating currents of low frequencies. Below 16 cycles nothing is audible in a telephone; but by this optical method the useful range of the telephone is extended to infra-sounds of very low frequencies such as are required by ocean cable telegraphy.

USE OF CIRCULAR REFLECTION FRINGES FROM PLANE PARALLEL MIRRORS

In the interference system heretofore described the glass plates are in contact, giving phenomena due to thin plates. A different arrangement has been used in which these plates are separated by several millimeters. The diagram, Fig. 6, shows a source of monochromatic light, S, partially reflected from the glass plate, G, placed at an angle of 45 degrees, down through the semitransparent mirror, P_2, consisting of a glass plate thinly silvered on the lower side, to the lower plate P_1, which is thickly silvered and polished on the upper side. Thence it is reflected perpendicularly upward, part of the light passing through the semi-transparent mirror, P_2, and part being reflected again back to the plate P_1. The former portion passes directly to the eye through the glass plate, G, and the latter goes over the same course after reflection between the two plates. When these plates are adjusted to parallelism circular fringes are perceived by the observer at E looking downward into the plates P_1 and P_2. This arrangement is a modified form of the Fabry-Perot interferometer as employed by Priest.[3]

The lower plate, P_1, is mounted upon the diaphragm, D, of a telephone. The observer sees a system of well-defined concentric rings which expand or contract as the distance between the plates changes, the central spot becoming alternately light and dark.

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[3] This Bulletin, 5, p. 110, on "A New Method of Determining the Focal Length of a Converging Lens."

If an alternating current of low frequency is applied, the circles visibly expand and contract alternately. As the frequency is increased the motion becomes so rapid that the whole field may appear uniformly illuminated, due to the persistence of vision. At 30 cycles some traces of motion are visible, but at 60 the field appears uniform if the current is sufficiently large.

When used as a telegraph receiver for alternating current, dots and dashes are read by noting the appearance and disappearance of the fringes. No apparent motion of the fringes, but merely their presence or absence in a fixed position, is seen by the unaided eye.

For low frequencies, four or five per second, such as are obtained in an ocean cable, the motion of the bands may either be followed by the eye or recorded photographically.

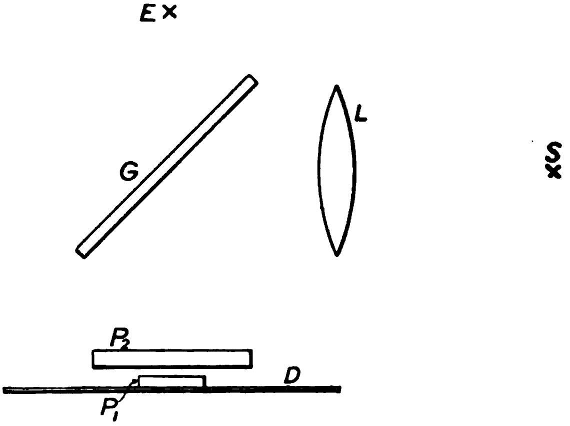

Fig. 6. Diagrammatic Arrangement of Apparatus for Circular Reflection Fringes. Pressure Varied by the Magnetic Field

In using this method, external sounds or jars vibrate the diaphragm and disturb the fringes. Even talking in the room is easily seen. No trouble from this source is experienced with the oscillatory band system formed by plates in contact. On the other hand, the fact that the diaphragm is perfectly free to vibrate in the circular fringe system makes this form very sensitive to alternating currents.

IV. PRESSURE VARIED BY THE ELECTRIC FIELD

The diagram, Fig. 7, shows a form of instrument for measuring changes of electromotive force. It is an electrostatic voltmeter, and may also be called an "optical condenser" in that the motion of the two condenser plates is observed visually as the electrostatic field between them is varied.

The flexible glass plates, A & B, 25 × 25 × 0.125 mm are each silvered on one side, the silvered sides being turned toward each other. A piece of paper, C, with a circular hole 2.5 cm in diameter separates the plates by a fixed distance, 0.05 mm, and leaves the condenser with air between the plates at the central portion. The two optically plane plates, as before, are placed upon the upper glass plate, and a pointer fixed to the frame holding the lower plate is brought to bear upon the upper plate. When the potential difference is changed from 0 to 20 volts an appreciable motion of the bands is observed. The volt-sensibility is increased, however, by an initial voltage which is slightly varied. A change from 106 to 108 volts produced an appreciable motion of the bands. The sensibility being proportional to the difference between the squares of the electric fields, the change in the first case gives 400 as the difference of the squares, and in the second case 428, values within the errors of observation. Although the sensibility is not high when applied to measuring small voltages, the energy required to produce a deflection is a small quantity. The computed capacity of this condenser is 0.000085 mf and the energy 0.108 ergs. This is roughly equal to the work of raising 1 milligram 1 millimeter.

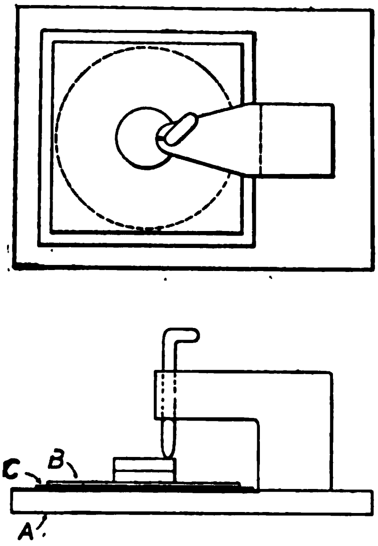

Fig. 7. *Optical Condenser. Pressure Varied by the Electric Field. One Unit*

OPTICAL CONDENSER PILE

Fig. 8 illustrates a pile of two condensers, one above the other, the upper carried on a small glass block, D, centrally located. The displacement of the top plate of the pile is amplified by this arrangement. The sensibility of the two condensers is practically twice that of one alone. A change of potential difference from 0 to 10 volts gives an indication with the condensers in parallel. The extent to which condensers may be added in this manner to advantage depends upon the mass of the moving parts.

This superposition of units is hardly possible in the electromagnetic form of instrument.

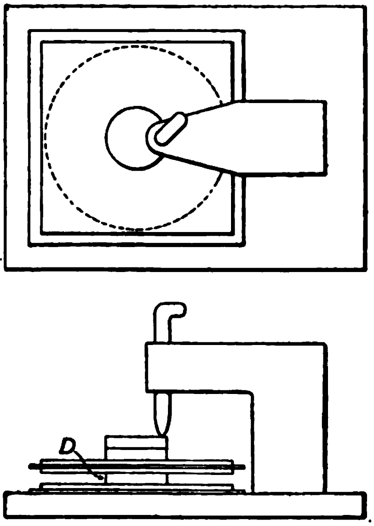

Fig. 8. Optical Condenser Pile. Pressure Varied by the Electric Field. Two Units

The volt-sensibility has been further increased by the following construction. A thick plane glass plate was silvered on the upper surface and one-half removed. A thin glass plate, 0.125 mm, was prepared in the same manner. A thin coat of lacquer was baked on one of the silver surfaces, and the thin plate laid upon the thick one with the silvered portions superposed. Bands are observed over the unsilvered area, although there were two coatings of silver and one of lacquer between the glass surfaces. The volt-sensibility is a change of potential difference from 0 to 3.4 volts.

COMPARATIVE SENSITIVITIES OF EYE AND OF EAR INSTRUMENTS

In using two of the physiological senses to observe phenomena, a comparison of their ultimate sensitivities is important. In making such a comparison, the frequency of vibration is a most important factor. The limits of sound frequencies which affect the ear makes this evident. These are of course not definite, but the lower is not far from 16 periods per second. At this limit the sensitivity to the eye is infinitely greater than to the ear. As the frequency is continuously increased, the sensitivity to the ear rises rapidly and the ratio falls. In the present state of our knowledge it is not known to what minimum value this ratio falls; but that there is a minimum at some particular frequency seems probable, since it is definitely known that the sensitivity to the ear again approaches zero at an upper limit in the neighborhood of from 20 000 to 40 000 periods per second.

The energy required to produce sounds of a definite amplitude rises rapidly with increase of frequency, and the properties of the atmosphere at these high velocities are far different from those at low velocities. Some of the energy required to vibrate a diaphragm is absorbed within the substance of the diaphragm itself, but at these higher frequencies the larger portion is transmitted to the atmosphere. By placing the diaphragm in vacuo, and observing its motion by interference methods, a given amount of applied energy must produce a very large increase in the amplitude. In this manner it seems probable that frequencies of vibration of solids may be observed and measured which are beyond the limits of the human ear.

The authors are indebted to Brig. Gen. James Allen, Chief Signal Officer of the Army, and Dr. S. W. Stratton, Director of the Bureau of Standards, for facilities furnished.

WASHINGTON, September 1, 1910.

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THE EFFECT OF PRELIMINARY HEAT TREATMENT UPON THE DRYING OF CLAYS

By A. V. Bleininger

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1. OBJECT OF THE WORK

This investigation has been undertaken for the purpose of looking into the possibility of using the excessively plastic clays, which on drying by any commercial method show great losses due to cracking and checking, by subjecting them in the crude state to a preliminary heat treatment before working them by the usual methods. There are, especially in a number of the Western States and on public lands, many clays of this sticky, heavy type which resist all ordinary modes of preparation. To this class of materials belong the so-called joint and swamp clays of the glacial regions of Ohio, Indiana, Illinois, Wisconsin, Minnesota, North Dakota, and other States and Territories.

In order to bring out clearly the various effects of such a preliminary treatment, extensive laboratory experiments have been made on small and large samples of widely differing plastic clays. Preheating, rather than other possible treatments, such as the admixture of sand or sandy clay or the addition of salts like sodium carbonate and sodium silicate, has been chosen, since the mixture with nonplastic materials like sand presupposes the presence of the latter within a reasonable distance, which frequently is not the case; on the other hand, the incorporation of soluble salts even in very small amounts may give rise to the appearance of disagreeable efflorescence on the surface of the ware. Still other means of dealing with this problem, such as the exposure of the dug clay to freezing during the winter or drying out in the summer, are not always practicable nor effective. Furthermore, mechanical drying has become a well-developed feature of many industrial processes, and its cost is in part compensated by the resulting regularity of the manufacturing process, the possibility of eliminating objectionable mineral detritus like gravel, lime pebbles, etc., and other desirable features.

2. GENERAL CONDITIONS OF DRYING

(a) The Plastic State.—The use of clay in the arts depends upon its plasticity, the property of retaining any shape into which it is molded, supplemented by its quality of hardening to a stone-like mass when dried and burnt. The cause of plasticity has been made the subject of elaborate discussions,[1] but as yet no exact explanation has been found for it. The most convincing experimental researches[2] ascribe the phenomenon of plasticity to the presence of colloidal substances which behave in many respects similarly to the typical colloids, such as silicic acid, ferric hydroxide, aluminum hydroxide, gelatine, glue, etc., in that they show the phenomena of hydrolysis, osmosis, adsorption, the ability to change from the gel to the sol form and vice versa in the presence of an excess of positive or negative ions, the property of shrinking in apparent volume down to a certain point proportionally to the loss of water, and the character of their dehydration and vapor tension curves.

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[1] For an excellent summary, see Heinrich Ries: Clays, Their Properties and Occurrence.

[2] Schloesing: Compt. Rend. **79**, pp. 376–80, 473–77, 1874. Van Bemmelen, Zs. f. anorg. Chemie, **18**, 14–36, *18*, 98–146. Cushman, A. S., The Colloid Theory of Plasticity, Trans. Am. Ceramic Soc., **6**, 65–78; On the cause of the cementing value of rock powders and the plasticity of clays, J. Am. Chem. Soc. **25**, 451–468. Ashley, H. E., Bull. 388, U. S. Geological Survey.

This view therefore appears to offer the most satisfactory basis for explaining the properties of clays and seems to reconcile some of the older theories which have been proposed.

We may then assume that the cementing substance of clays is represented by some colloid, not necessarily of a definite chemical composition nor always of the same physical character, which possesses a more or less marked micellean structure in which water is held in the free and absorbed condition. Owing to the fact that clays are of different origins and are subjected to various modifying conditions during and after deposition, it is very probable that they are made up of colloidal substances, which vary widely as regards their physical structure. Thus the clay substance of the light burning, plastic clays is bound to differ considerably from that of the red burning surface clays and shales, not only in amount, but in character as well. Again, in many clays, especially those of primary origin, the transition of the crystalline matter to the colloidal condition still goes on, due to weathering and other agencies. This applies particularly to materials of the kaolin type. In other types the colloidal clay substance, has been in part "set" by certain geological conditions, though not irreversibly. In these a close and dense structure prevails which does not absorb water until the latter is forced into the pores by grinding and pugging. Clays of this type therefore show but a feeble initial plasticity, but become workable by energetic mechanical treatment. Fire clays and shales are especially apt to show this kind of behavior.

It seems to be a fact, however, that plasticity as measured by the ability of the clay to be molded, and to flow through dies, is dependent upon the development of this water-saturated micellean structure.

Equally important with the degree to which this condition of the cementing substance is developed is the amount and character of the nonplastic constituents of the clay which affect the plasticity as well as the resulting density of the clay body. This inert mineral matter, consisting of grains of quartz, feldspar, mica, limestone, pyrites, augite, hornblende, etc., not only dilutes the plastic clay substance, but by virtue of its granulometric composition, becomes a prominent factor in determining the resulting plasticity, drying shrinkage, ease of drying, and final density.

Since it is necessary to assume that each grain of nonplastic material be surrounded by an envelope of plastic substance, it is readily seen that the extent of the surface exposed by these particles is of great importance in regard to the plasticity and capillary structure.

Considering the subject theoretically and assuming that the crystalline grains are spherical in shape and fill a certain unit volume as compactly as possible, it can easily be shown that the total pore space remains constant at 30.3 per cent of the total volume, but that the surface exposed by the grains varies. If, for instance, the size of the particles were reduced from a diameter of 0.75 mm to 0.25 mm, the total surface exposed under the above conditions would be three times as great as before. On assuming a reduction in size from 0.75 mm to 0.125 mm, the surface would become six times as large. Or, speaking more generally, the surface exposed by different sizes of grain would be inversely proportional to the diameter. The surface of compactly arranged spherical particles in unit volume would vary as 4.1845 $(1 \div d)$, i. e., proportionally to the product of a constant and the reciprocal of the diameter.

Assuming that each particle must receive an envelope of plastic matter of uniform thickness, it is evident that the smaller grains would require a larger amount of this material than the particles of greater diameter. It is conceivable, therefore, that a definite volume of clay might prove insufficient to coat a large number of very fine grains, while the same quantity would be ample for an equivalent volume of larger, nonplastic particles. In the latter case, therefore, we should expect to find greater mobility of the mass as a whole, owing to the thicker enveloping layers which are made possible, i. e., the larger grains reduce the plasticity of the clay less than the finer. By analogy it appears, then, that the tensile strength of the clay would be the greater the larger the average size of the granular matter, provided the total amount is kept within proper limits.

If the nonplastic particles are not uniform in size, it is evident that the pore space between the granular skeleton is decreased and it is possible to assume a combination which will result in maximum density. Of two sands mixed with the same weight of clay, the one producing the smaller volume of clay-sand mixture will show the greater density. The granulometric relations holding between the various sizes of granular matter in clay are similar to those applying to cements, as shown by the experiments of Feret,[3] although, however, there are certain differences inherent in the nature of clay.

It is seen, hence, that not only the amount and character of the colloidal clay matter, but also the amount and sizing of the nonplastic constituents govern the resulting plasticity. In addition, other factors are bound to be of more or less influence, such as the shape of the nonplastic particles, the presence of organic matter, various salts, bases, or acids.

(*b*) **The Evaporation of Water from Clay.**—In making up dry clay with water to form a plastic mass which may be shaped and molded, the resulting volume is somewhat greater than the sum of the volumes of clay and water. In this condition the clay particles, both plastic and granular, are surrounded on all sides by a film of water, while small pools or drops fill the cavities and pores between the grains. A tortuous system of capillaries is thus established which are wider in some places and narrower in others. When placed in an atmosphere saturated with moisture, equilibrium conditions are reached when no flow of water whatever takes place in these minute channels. As soon as the humidity is lowered, however, evaporation begins to take place on the surface, and every particle of water thus removed must be replaced through the capillary channels from the interior. The rapidity of this movement depends upon the structure of the clay—i. e., whether the capillaries are fine and intricate or coarse and short—

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[3] Bull. de la Societe d'Encouragement, **2**, p. 1604; 1897.

and upon the temperature and humidity of the outside air. Open structure, high temperature, and low humidity result in maximum capillary flow and vice versa. Since the spongelike colloidal matter with its immense surface and fine pores offers the greatest resistance to the passage of water, it is obvious that in highly plastic clays the movement of the water through the capillaries must be very slow, it having been estimated that the resistance to this flow is inversely proportional to the fourth power of the diameter of the channels. The capillary flow continues to grow weaker until the films become very thin and finally break altogether.[4] The water remaining within the colloidal interstices and within the pores in isolated films is expelled with increasing difficulty, and, owing to its low vapor pressure, requires a high temperature for its complete expulsion.

Considering now the drying of clay from the experimental standpoint, the relation between shrinkage and loss of water during this process might be examined in a specific instance. The curves of figure 1 represent the linear shrinkage of a clay sphere in terms of the diameter in the dry state and the loss in weight expressed in per cent of the dry weight plotted against the time of drying in hours.[5] The sphere was 7.11 cm in diameter in the wet state and was carried through the drying stage in an oven maintained at a constant temperature of 60° C. When a loss in weight was no longer observed, the temperature was raised to 120°, and finally to 200°. In each case the same temperature was maintained until the weight was constant. It is noted that down to a certain point the rate of shrinkage is proportional to the rate of the loss in weight, then the shrinkage becomes less than the loss of water, and finally it ceases, while the clay continues to evaporate water. The point at which shrinkage no longer takes place and where the clay grains are supposed to come in contact with each other is used to discriminate between two kinds of water. On drawing through this point a line parallel to the abscissa, the water lost above it represents the shrinkage and that below it the so-called pore water. Neither term is rigidly exact, since in some materials, especially

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[4] Studies on the Movement of Soil Moisture, E. Buckingham, Bureau of Soils, Bull. No. 38, p. 41.

[5] E. F. Lines, Note on the Drying of Clays, Trans. Am. Ceram. Soc., **10**, p. 146.

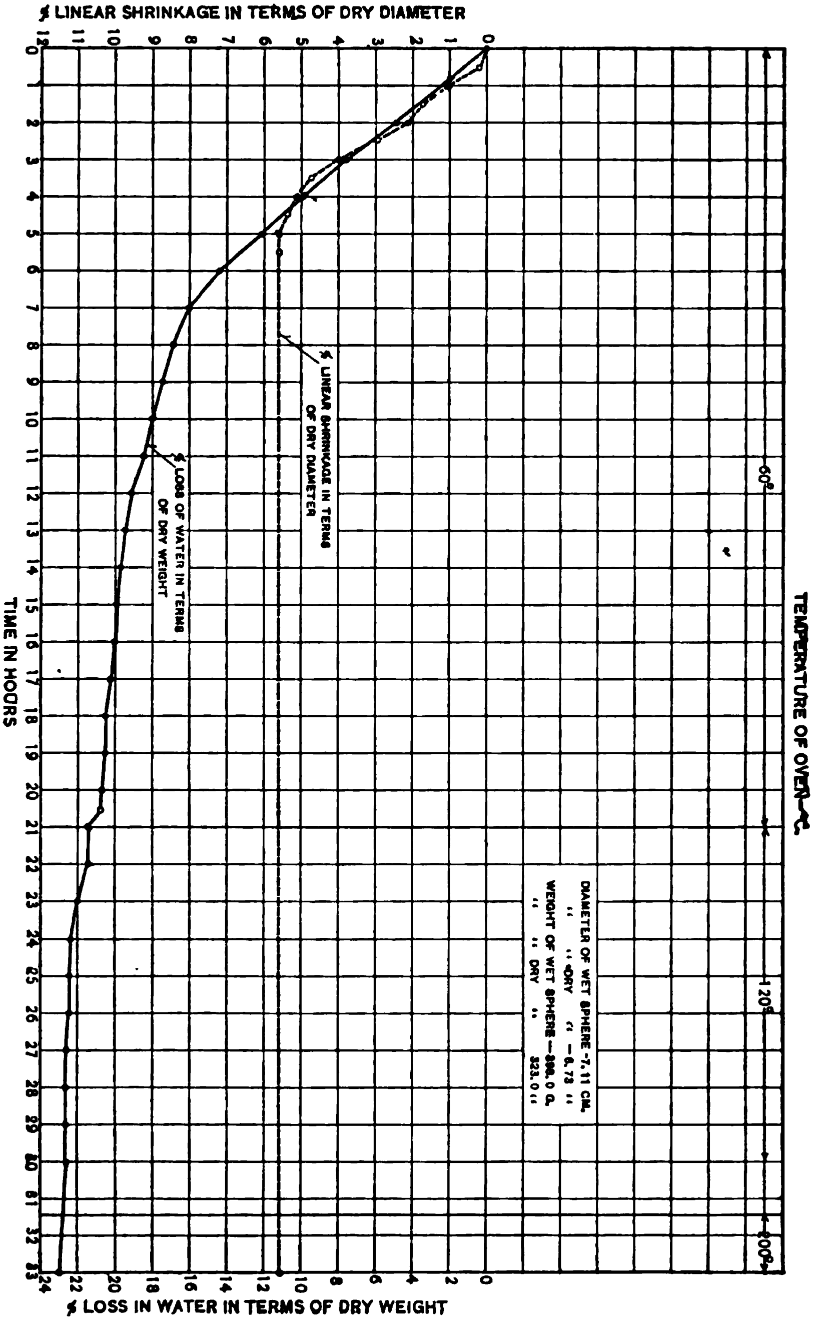

Fig. 1.—Relation between loss of weight and shrinkage in the drying of clay.

of the porous, feebly plastic type, the first loss in water is not necessarily equivalent to the shrinkage, and again the pore water includes also the adsorbed water and the water of imbibition.

The loss of water continues at a decreasingly slower rate until the weight is constant at the given temperature. Upon raising the temperature more water is expelled and this continues until finally the last residual portion is set free. The decreasing rate of the water loss is evidently due to the decreased capillary conductivity[6] brought about by the reduction in the number of the capillary paths, the effect of surface tension and adsorption phenomena and with them the decrease in vapor pressure.

Upon bringing clay dried at atmospheric temperature again in contact with water the latter will at once be absorbed and the air within the network of capillaries expelled with the evolution of heat. The colloidal matter will swell in taking up the water so that not only the pores of the clay mass become filled, but a certain amount of the water is absorbed into the micellean structure. Clay invariably takes up water more readily in the dry than in the moist condition.

The water of the clay, as may be inferred from the fact that its vapor tension constantly becomes smaller, is by no means expelled completely when the specimen has reached the "bone-dry" condition at the temperatures of the commercial dryers. According to the nature of the clay and its structure more or less mechanical moisture remains which is given off only at higher temperatures. This so-called hygroscopic water which is held so tenaciously usually remains to be driven off in the kiln. It is evident therefore that this moisture is readily absorbed by dry clay from the air. In Table I the results of drying 12 clays at temperatures from 60°–200° C are shown; at each temperature the drying was continued until the weight became constant.

The increase in volume on the addition of water to dried clay is practically equal to its previous shrinkage on drying, provided the material has not been subjected to a higher temperature while in the dry state. If this has been the case the amount of water again taken up and the increase in volume will be distinctly less, and this is the more pronounced the higher the heating has been carried.

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[6] Edgar Buckingham, Bull. 38, Bureau of Soils, p. 43.

TABLE I

Loss in Dry Weight on Heating

In per cent of the dry weight

	1	2	3	4	5	6	7	8	9	10	11	12
Loss at 200°	0.23	0.11	0.10	0.42	0.10	0.48	0.49	0.06	0.06	0.33	0.58	0.30
Loss at 150°	.17	.005	.16	.004	.10	.006	.34	0	.06	.001	.40	.12
Loss at 110°	.25	.11	.14	.40	.32	.32	.18	0	0	.11	.27	.005
Loss at 100°	1.56	.75	.93	1.17	1.30	1.28	1.36	.277	.24	.64	.85	1.20
Loss at 60°	59.84	20.17	37.92	38.84	45.61	42.40	29.19	28.72	45.87	24.59	30.72	49.80
Total loss	62.05	21.15	39.25	40.83	47.43	44.49	31.56	29.06	46.23	25.67	32.82	51.43

This is in accord with the results obtained by Van Bemmelen [7] with silicic acid gels in which he noted a distinct lag in the absorption of water on rehydration. He found that at first the liquid between the pores of this colloidal material left at a rate corresponding to the evaporation of free water. This was found to hold true for a water content of from 120–125 molecules.

Below this point the liquid within the micellean interstices evaporates at a continually slower rate owing to the narrowing of the capillaries. Also the vapor tension of the colloid decreases steadily, corresponding to the decrease in the content of absorbed liquid. At the same time constant changes occur in the physical condition of the substance which are slow at ordinary but accelerated at higher temperatures.

Van Bemmelen studied the inversion points by placing the silicic acid gels into desiccators containing 36 concentrations of sulphuric acid and hence corresponding to 36 aqueous tensions. He found several inversion points in the resulting dehydration curve. First, the substance becomes dull and fluorescent, then white like porcelain, and finally opaque white, like chalk, without gloss. This inversion changes the dehydration curve, since for a distance it runs parallel to the abscissa. The capacity to hold water then decreases more rapidly than before the inversion point. On continuing the dehydration still further the dimness disappears just as it appeared. The gel becomes porcelainlike, of bluish fluorescence, and finally as clear as glass, remaining thus until the final dehydration. Also, when the gel is at once exposed to higher aqueous tensions, after the inversion, it becomes gradually homogeneous and clear as glass. These inversions may be repeated, and they are hence reversible under certain conditions. It is evident therefore that certain changes occur in the micellean structure of the colloid at these inversion points forming new coagulations which disturb the continuity of the dehydration curve.

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[7] Zs. f. anorg. Chem. *18*, 14–36; *18*, 98–146; 20, 185–211.

By taking now the silicic acid pats which have been carried on to the lowest aqueous tension (most concentrated sulphuric acid), and placing them in the desiccators containing the more dilute sulphuric acid solutions rehydration takes place. Van Bemmelen in again plotting the molecules of water at each stage against the aqueous tension then found that the dehydration curve was not reproduced, but that a distinct lag was observed analogous to hysteresis—i. e., while a certain aqueous tension in the case of the fresh silicic acid corresponded to a certain amount of water, the same tension in the rehydrated substance was equivalent to a smaller amount of water.

While a homogeneous substance like silicic acid is not strictly comparable to a heterogeneous mixture like clay, certain observations bearing on the one might be utilized in connection with the other. The question which naturally arises is to what extent the plasticity of clays and its related phenomena, such as shrinkage, are reversible on heating clays up to temperatures still considerably below the dehydration point at which practically all clays lose their working quality completely. It has generally been understood that, up to the temperature at which the combined water is expelled, the plasticity and water absorption are to a large extent reversible; that is, the clays are able to resume a large share of their original plasticity. On the other hand it has been realized that a certain lag is observable since in pottery work it has been found that the dried ware which is again returned to the plastic state does not possess the same working quality on the jigger that it possessed originally. Whether on sufficient working and aging the clays would resume their initial plasticity is an open question, though it would seem very likely that this would be the case as far as the usual dried clay is concerned.

(c) **Shrinkage.**—In a general way the conditions governing the rate of drying of clays have been indicated. As has been pointed out the true volume of the dry clay plus the volume of water required to produce plasticity is less than the resulting apparent volume of the mass. This may be due to air mechanically inclosed, to flaws in molding, and volume changes due to the action of dissolved salts upon the clay gel.

In a series of experiments the volume changes taking place on working up a number of dry clays have been measured very carefully, the results of which are compiled in Table II.

TABLE II

Volume Changes in Working Dry Clays

Clay	Spec. Gr. of clay dried at 100°C	Weight of dry clay, grams	Weight of water added, grams	Volume of wet test piece, cc	Volume of clay plus volume of water, cc	Increase in volume in per cent of volume of test piece
Plastic high-grade clay, Tennessee	2.440	30	12.04	24.80	24.33	1.89
High-grade plastic clay, New Jersey	2.590	30	11.20	23.80	22.78	4.29
White plastic fire clay, Texas	2.587	30	11.78	24.30	23.38	3.53
Common glacial clay, Minnesota	2.464	30	11.51	23.80	23.68	0.50
Common glacial clay, Illinois	2.599	30	19.00	21.20	20.54	3.11
Alluvial clay, very plastic, Ohio	2.504	30	18.46	21.50	20.44	4.93
Common glacial clay, New York	2.703	30	18.41	19.70	19.51	0.96
High-grade plastic clay, Tennessee	2.585	30	13.96	26.90	25.57	4.94
Glacial clay, very plastic, North Dakota	2.655	30	15.80	28.00	27.10	3.21
High-grade kaolin, England	2.583	30	10.32	23.10	21.93	5.06

A short experimental series was also undertaken for the purpose of showing the rate at which several clays lose their residual water when subjected to conditions of decreasing vapor tensions. Five clays were made up into thoroughly homogeneous plastic pastes and placed into tared capsules provided with tight fitting lids and weighed.

The clays thus treated in the order of their apparent plasticity and difficulty of drying are as follows:

No. 1. An impure, exceedingly plastic glacial clay from Fort Pierre, N. Dak.

No. 3. A ball clay from Whitlock, Tenn., through the Potter's Supply Company.

No. 6. A very plastic kind of fire clay from Edwards County, Tex.

No. 7. A plastic glacial clay from Albert Lea, Minn.

No. 10. A high grade English china clay, Pool No. 1.

Of each clay five such samples were prepared. Five concentrations of sulphuric acid were then made up, of which a sufficient quantity was poured into each of five desiccators. These solutions of sulphuric acid represented final vapor tensions of from 12 to 0.15 mm, at 25° C, taking the water given off by the clays into account. After weighing the closed capsules containing the clay samples, which averaged about five grams, the covers were removed and one pat of each clay placed in every desiccator. They were allowed to remain in these for 21 days when they were again weighed. The room temperature fluctuated between 21° and 26° C. It was thus possible to compare the water losses suffered by each clay for the difference in vapor tension given above by subtracting from the percentage of water at 12 mm the percentage contents at the lower tensions. In this way the curves of Fig. 2 were obtained. In these only the residual water is considered, beginning with the amount of water left under a vapor tension of 12 mm to which all clays were subjected. It is at once observed that the amount of the residual water varies, being largest, 5.3 per cent, in the case of No. 1 and lowest, 0.85 per cent, for No. 10. The more plastic and "sticky" clays, therefore, show the highest water loss for the given difference in vapor tension. It is evident from this that the rate of drying at a constant temperature likewise varies for the different clays being slowest in the most plastic materials. These facts indicate not only varying amounts of plastic clay base in the different clays, but deep-seated variations in the micellean structure itself as well, since it is hardly probable that the larger content of residual water remaining in an impure material such as No. 1 could be attributed to a higher content of theoretical clay substance ($Al_2O_32SiO_2.2H_2O$) than is contained in the far purer clays Nos. 3, 6, and 10.

After having been replaced in the desiccators the samples were again weighed after three months and were found to possess practically the same weight. It seems thus that the conditions of equilibrium had been approached sufficiently close for the purpose of the experiment.

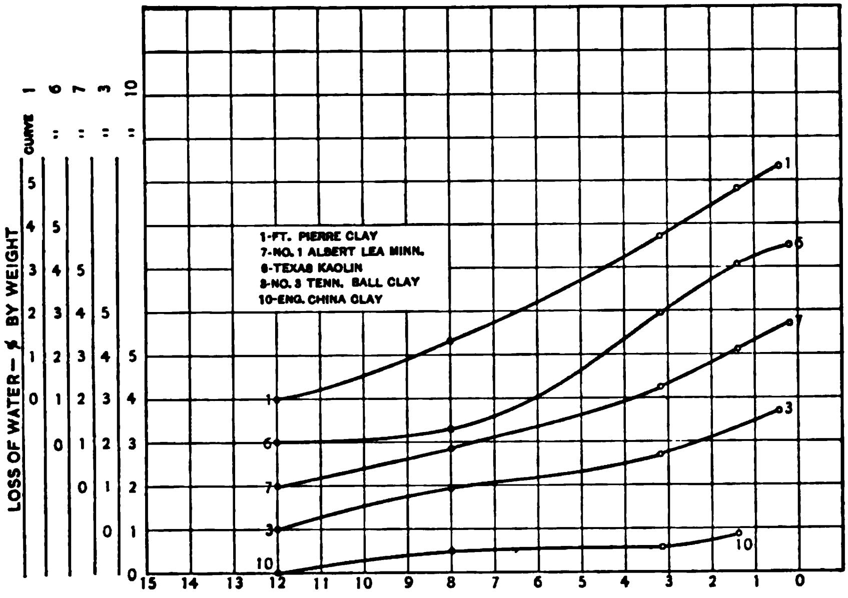

Fig. 2.—*Relation between loss of water and vapor tension of fire clays.*

The drying shrinkage of a homogeneous clay body of geometrical symmetry, free to contract, is uniform in all directions. The most accurate valuation of shrinkage is obtained by means of volume measurements, though for practical work the linear dimensions in the wet and the dry state will suffice. The linear shrinkage is readily deduced from the volumetric values by the relation:

$$\% \, l = \frac{\sqrt[3]{v_1} - \sqrt[3]{v_2}}{\sqrt[3]{v_1}} \, 100$$

where v_1 and v_2 are the volumes in the wet and the dry state, respectively, and l is the linear shrinkage in terms of the wet length. If the linear contraction is desired in terms of the dry length, the denominator of course becomes $\sqrt[3]{v_2}$. The assumption commonly made that the volume shrinkage is equal to three times the linear shrinkage is not sufficiently exact even for practical purposes. If the initial (wet) volume is assumed to be unity and a = linear shrinkage, the dry volume becomes $(1-a)^3$, or $1-3a+3a^2-a^3$. The shrinkage, therefore, $=3a-3a^2+a^3$, in which the term a^3 may be neglected, but not $3a^2$.

Owing to the fact that the amount of water used in making up the same clay is not constant, the apparent volume of a lump of a definite weight of dry clay varies somewhat even with the most painstaking manipulation. Likewise the pore space remaining in the dried material does not remain the same in each case. For this reason it has been thought advisable to express the volume shrinkage in terms of the true clay volume; i. e., weight of dry clay divided by its density in the powdered state.

In the study of the drying behavior of clays two factors are of considerable significance, viz, the amount of water required to produce a plastic mass and the shrinkage on drying. Ordinarily the more plastic and difficultly drying clays require the highest amounts of water and show the greatest drying shrinkage, although there are exceptions to the rule. Some materials, owing to peculiar conditions, such as excessive fineness of the granular matter, may dry more difficultly with lower water of plasticity and shrinkage than clays with higher water content and shrinkage.

In seeking for approximate values expressing the drying behavior of a clay by means of an experimental test it is necessary to know the total amount of water required to develop plasticity, the volume shrinkage, and the time required to evaporate the shrinkage water at a constant temperature. This means that the length of the test specimen must be carefully measured at short intervals. Then, knowing the time required to reach the point at which shrinkage ceases, and the total shrinkage, an estimate may be made of the drying behavior of the clay by multiplying together the values obtained for time and shrinkage. This numerical expression is inversely proportional to the ease with which it dries.

For the purpose of illustration the following description of a similar experiment might be cited.[8] Spheres of clay 7.11 cm in diameter were made, maintained for some time under conditions of moisture saturation in order to establish a condition of equilibrium, and then placed in an oven at a constant temperature of 60° C, regulated by means of a thermostat. The diameter of the sphere was measured from time to time by means of a vernier caliper. Thus the point was determined at which shrinkage ceased. A shale was found to possess a linear shrinkage of 4.0 per cent in terms of the diameter in the dry state, and it lost its shrinkage water in 4 hours. The factor in this case would be $4 \times 4 = 16$. Similarly, a washed No. 2 fire clay showed a shrinkage of 6.5 per cent and lost its shrinkage water in 5.1 hours, giving a value of $6.5 \times 5.1 = 33.15$. Finally, a fine-grained, glacial clay, very difficult to dry, possessed a shrinkage of 8.5 per cent and ceased contracting in 8.9 hours, resulting in $8.5 \times 8.9 = 75.65$.

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[8] E. F. Lines, Trans. Am. Ceram. Soc. *11*, 146.

Since these measurements were made under strictly comparable conditions as to drying temperature, initial size, and shape (spherical) of the test pieces, the numerical values are inversely proportional to the ease with which the clays dry in practice. The actual drying behavior of these clays was well expressed by the factors, the shale being the easiest and the glacial the most difficult to dry under commercial conditions.

Practically the same results could be obtained by determining the initial diameter and weight of the test piece, weighing it at frequent intervals, and measuring the size in the dried condition. The time when the calculated weight of shrinkage water (which should be equal in volume to the volume shrinkage) has been evaporated could be readily obtained from the time-weight curve.

The rate of drying has some influence upon the shrinkage of clays, inasmuch as rapid heating is said to result in a lower total contraction. As far as known to the writer, no experimental proof of this statement is at hand.

3. DIFFICULTLY DRYING CLAYS

Clays are subject to two kinds of difficulties in drying which are opposite in character. They may give trouble, due either to an excess of plastic material or to a deficiency of it. In the first case the system of capillaries is so extremely fine that the flow of water through it is very slow and becomes the more restricted as shrinkage progresses. Owing to the fact that such clays show a very large contraction in volume, the capillary channels necessarily become smaller and smaller on drying, thus causing the difficulty of expelling the water to increase.

(a) Causes of Cracking.—The result is inevitably that the rate of surface evaporation is greater than the flow of water toward the surface, a condition which gives rise to strains and more or less marked ruptures.

In the second case the amount of clay bonding matter is so low that the body does not possess the tensile strength needed to withstand the strain caused by the closing up of the particles near the evaporating surface. The result of this condition is that the clay gives way and cracks.

In order to overcome these two classes of difficulties, some remedial measures are available. These are for the excessively plastic clays dilution by means of nonplastic materials like sand or ground, calcined clay (grog), or drying of the ware under carefully regulated conditions with special reference to the maintenance of a high humidity in the drying until the clay has become uniformly heated throughout, or by using the preliminary heating treatment which is the subject of this work.

As regards weak clays, lacking in plastic clay matter, the means open for overcoming the difficulty consist in developing the available plasticity to its maximum by means of storing in the wet condition, by grinding and thorough pugging, by the use of slightly acid tempering water (in some cases), and finally by the incorporation of a more plastic material, which offers the most positive solution of the case.

(b) Effect of Nonplastic Materials.—The addition of granular, nonplastic material to an excessively plastic clay is made for the purpose of improving the working quality by reducing its "stickiness," decreasing the drying shrinkage, and with it the tendency to warp and crack in drying, and of lowering the kiln loss due to strains caused in drying and the impermeability of the dense clay to air needed for the oxidation of the organic matter present in all argillaceous materials. Nonplastic matter, intimately blended with the clay, thus exerts a decided influence upon the working qualities of the latter, affecting the penetration of water into the pore system, the shrinkage in drying and burning, as well as the porosity in the dried and burnt condition. Its effects, hence, are far reaching, since they are intimately connected with the final use of the product, its resistance to weathering agencies, abrasion, etc.

When any granular, nonplastic material of uniform size is incorporated in a strongly plastic clay several effects may be observed. The volume shrinkage, providing the same percentage by volume of water is maintained, may be found to increase up to a certain content of the nonplastic constituent, but beyond this point it will decrease. The density of the clay mass may thus be said to increase to a maximum. After passing it the shrinkage decreases while the porosity rises. This effect is brought out more or less clearly according to the granulometric composition of the nonplastic material added and the initial content of such material in the clay.

It is evident that on introducing small amounts of a nonplastic material into a plastic clay the spongelike matrix envelops the hard grains and the total pore space per unit volume, assuming that the sand, or whatever material may be added is free from pores, has been decreased. If the total water content be kept constant, some of the pore water therefore becomes shrinkage water, with the result that the contraction in drying is increased. From this it follows that since the pore water, and hence the pore space, has been decreased in volume the density of the mass must have increased. Upon continuing the addition of nonplastic material the point is reached when contact is established between the incorporated grains, and therefore some of the shrinkage water again becomes pore water. Shrinkage therefore decreases from this point on and the porosity increases.

If in the case of a difficultly drying, exceedingly plastic clay it is decided to add sand for the purpose of making it easier to dry, this addition should be carried beyond the point of maximum density, so that a larger pore space, and hence an increased evaporation and outlet area is produced.

In tracing the effect of nonplastic matter the assumption has been made above that the water content be kept constant. If this condition is not fulfilled but the attempt is made to maintain constant consistency, the above facts still hold, although the effects are not so marked. In determining the drying shrinkage of five low grade, plastic clays with varying percentages of a very uniform sand (20–30 mesh), and at the same time aiming to keep the consistency constant, it was possible in each case to fix clearly the point of maximum density.

The size of grain of the nonplastic material is necessarily an important factor in the resulting density and the system of pore spaces. Fine-grained sand, for instance, at the point of maximum density will result in a more porous structure than coarser grained at the same point. With equal water content a fine nonplastic will bring about a stiffer consistency than coarser-grained material. As regards a mixture of grains of various sizes, the same statements hold that have been made with reference to the natural granular constituents of clays.

4. PREHEATING

(a) The Clays Used in the Experiments.—Since this bulletin deals solely with the study of the preheating treatment of clays and its effect upon clays, a detailed consideration of other methods bringing about similar results can not be undertaken at this time.

For the purpose of the investigation 14 clays were selected, covering a wide range of chemical and mineralogical compositions. Their character is indicated by the following descriptive remarks:

No. 1.—An exceedingly plastic clay, very similar in behavior to bentonite, from Fort Pierre, N. Dak. It is impossible to dry this material without cracking. Its fineness of grain is remarkable. Apparently it contains some calcium carbonate in a state of extremely fine subdivision.

No. 2.—St. Louis fire clay, Highland Fire Clay Co., St. Louis, Mo. A high-grade fire clay, but lacking in plasticity, owing to insufficient reduction of clay grains. Grinding at once improves the plastic quality simply by disintegrating the coarser, wax-like clay particles.

No. 3.—Tennessee ball clay No. 3 (Potter's Supply Co.), from Whitlock, Tenn. A clay of great plasticity and bonding power. It dries without difficulty excepting when fabricated into large pieces, when care must be taken to prevent cracking by maintaining a high humidity during the initial stages and by keeping the drying temperature down as low as possiple.

No. 4.—Prall sagger clay, Woodbridge, N. J., a decidedly plastic material of excellent bonding power and of safe drying behavior. It contains coarser grains of quartz.

No. 5.—Pike's No. 20 ball clay, a high-grade English plastic material which when used alone has a decided tendency to warp and which when made up into large pieces must be dried with great care to prevent cracking. Its bonding power, which makes it valuable, is very high and by some it is considered the strongest material of this kind on the market.

No. 6.—Texas kaolin, "Lone Star" brand, from Edwards County, Tex. A fire clay consisting of clay grains and extremely fine clay matter. Grinding increases the plasticity of this clay immensely and in this way it is capable of great improvement by the reduction of the comparatively coarse clay grains. It does not seem to give trouble in drying.

No. 7.—An extremely fine-grained glacial clay from Albert Lea, Minn., of considerable plasticity, but troublesome to dry.

No. 8.—Joint clay, from Urbana, Ill. A plastic glacial clay, difficult to dry, due not so much to great fineness of grain as to "joint" structure which is indicated by the fact that bricks made from it on drying split vertically into more or less irregular cubes.

No. 9.—Albany slip clay, a fine-grained glacial clay from northern New York, low in bonding power, but showing sufficient plasticity.

No. 10.—English China clay, J. Poole No. 1, considered a high grade of kaolin, not commonly imported, of excellent plasticity and yet producing a fine white color.

No. 11.—Joint clay, Peoria, Ill., a typical fine-grained glacial clay, giving some trouble in drying.

No. 12.—A typical alluvial clay from Groveport, Ohio, of decided plasticity, somewhat troublesome to work and dry. Probably quite high in ferric oxide, since on burning a fine red color is developed.

No. 13.—A No. 2 fire clay, highly impregnated with ferric oxide, from Athens, Ohio, very plastic, with some tendency to crack in drying though excellently suited for admixture with shale owing to its ease of slaking down on contact with water.

No. 14.—A glacial, calcareous clay from Heron Lake, Minn., possessing good plasticity and working properties though somewhat too fine grained for drying when made into larger pieces.

In the effort to correlate the drying shrinkage with the fineness of grain and the general plastic behavior of these different clays the following determinations were made:

1. Drying shrinkage in the normal condition.
2. Fineness of grain by means of the mechanical analysis.
3. Resistance offered by mixtures of clay and water to the passage of a paddle in the Stormer viscosimeter.

(b) **Drying Shrinkage.**—In determining the drying shrinkage of the clays they were made up with water to "plastic" consistency, which, in spite of its apparent indefiniteness, is a condition fairly sharply defined in the hands of an experienced operator. Owing to the fact that there exist no other means of maintaining a constant consistency, it was necessary to depend solely upon the judgment of the manipulator. In some preliminary experiments, however, it was shown that the water content representing good working quality could be checked for the same clay with satisfactory accuracy since at approximately the proper working consistency the clays are quite sensitive to a deficiency or excess of water. This property varies somewhat with different materials, very plastic clays being less sensitive to variations in water content than those higher in nonplastic matter. After having been allowed to stand over water for 24 hours the clays were molded by hand into approximately cylindrical test pieces which were at once weighed and their volume determined. The weighing was done in closed tin cylinders to prevent loss by evaporation. The volume of each cylinder was determined by immersion in petroleum making use of a narrow-necked flask and obtaining the volume of liquid displaced by means of a burette calibrated to 0.1 cc which permitted of easily reading to 0.05 cc. The weight of the clay cylinders varied between 20 and 35 grams and the volumes from 12 to 22 cc. After the determination of weight and volume the test pieces were dried at 60° till the weight was constant and finally at 100°. The dry specimens were then weighed and immersed in melted paraffine at a sufficiently high temperature so that the liquid penetrated into the interior, but dripped off completely on removing the piece from the bath. When cool the cylinders were placed in petroleum for several hours and the volume determined as before.

In Table III the volume shrinkage of the clays in terms of the dry volume of the cylinder and of the true volume of the clay as well as the linear shrinkage in terms of the wet length are compiled. For purposes of comparison the shrinkage referred to the true clay volume is to be preferred owing to the variable factor of the pore space which depends upon the character of the clay, the method of manipulation, etc.

The shrinkage expressed in terms of the real clay volume is readily calculated from the relation:

$$s = \frac{d\,(v_1 - v_2)}{w} \text{ where—}$$

s = volume shrinkage in terms of the true clay volume.
d = specific gravity of powdered dry clay.
v_1 = volume of clay cylinder in the wet state.
v_2 = volume of clay cylinder in the dried state.
w = weight of the dried cylinder in grams.

TABLE III

Shrinkage of Various Clays

No. of clay	Specific gravity of powdered dry clay	Volume shrinkage in per cent of volume of dry test piece	Volume shrinkage in per cent of true clay volume	Linear shrinkage in per cent of the wet length
1	2.451	68.57	99.80	15.97
2	2.551	23.40	30.30	6.77
3	2.770	38.10	60.73	10.20
4	2.596	34.50	54.80	9.41
5	2.577	48.19	61.96	12.28
6	2.510	36.80	60.10	9.92
7	2.580	36.20	49.00	9.79
8	2.603	30.30	41.85	8.44
9	2.784	16.90	25.80	5.07
10	2.476	21.05	34.80	6.17
11	2.575	32.20	49.00	8.89
12	2.680	37.86	51.09	10.15
13	2.768	38.00	49.05	10.18
14	2.645	27.30	42.65	7.72

The specific gravity of the clays was determined by means of the pycnometer with the usual precautions as regards exhaustion of the air and correcting for temperature.

The linear shrinkage was calculated from the condensation in volume.

The clays examined, with the exception of three, the Highland fire clay, the Albany slip clay, and the English china clay, belong to the more difficultly drying materials when made up into heavier products. The clay from Fort Pierre, N. Dak., is in a class of its own, and it appears to be impossible to dry it under any conditions.

(c) **Mechanical Analysis.**—The mechanical analysis as practiced by agricultural and ceramic investigators consists in the separation of grains of certain arbitrary size limits by means of sieves and further separation by means of sedimentation, elutriation or centrifugal action, water being used as the medium of flotation. For the purpose of the ceramist the Schulze apparatus, in which the separation of the grain is effected by the method of elutriation, is commonly used and meets the technical requirements owing to the simplicity and convenience of its arrangement. It consists of three tin-lined copper cans with conical bottoms, 2, 5, and $6\frac{15}{16}$ inches in diameter, respectively, through which water is allowed to flow at a constant rate, 176 cc per minute. It is readily seen that this results in the greatest velocity in the narrowest and the lowest in the widest can. With the diameters of the cans and the volume of water given, the largest particles settle in can No. 1, averaging about 0.0577 mm diameter, the next smaller in No. 2, averaging about 0.0354 mm, while in No. 3, the average size approximates 0.0167 mm. Particles still finer, about ±0.005 mm, are carried off by the overflow.

The average size represents the microscopic measurement of 50 particles of each sediment and is the arithmetical mean. In this connection the difficulty of obtaining the true mean diameter is fully realized, but for the work in question this method has been preferred to the method of mean integrals, since it was not desired to calculate a surface factor. After the water escaping from the third can appears to be clear the cans are emptied by siphoning down to the conical bottom. The water and clay in this part of the cans is washed out, evaporated to dryness, and weighed. The amount of the finest particles is obtained by difference. Before being placed in the elutriating apparatus the sample of the dry clay, the amount of which is usually 50 grams, is made up with water to form a thin slip, deflocculated by the addition of caustic soda or sodium oxalate according to the nature of the clay and mechanically shaken for one hour. The clay suspension is then passed through a series of small conical sieves, telescoped together, ranging from 20 to 120 mesh. After washing and drying the residues on each sieve are weighed. .The material which passes the 120-mesh sieve is collected and introduced into the elutriating apparatus.

The water flowing through the cans is taken from the tap, but is filtered through beds of sand and charcoal. Its temperature is kept constant by heating to a certain temperature and regulation by means of a thermostat. The separation of the sediments is considered successful when the residues dry down without cracking. If the latter occurs, some of the clay matter has been retained, and the test is repeated, the clay sample being deflocculated more thoroughly or another reagent is employed such as sodium oxalate. In extreme cases the deflocculating solution is dropped slowly into the first can for a number of hours. Certain precautions must be observed in the operation of the elutriating apparatus, such as to start with a reduced flow of water until the first can appears to be comparatively clear when the current is brought to the standard velocity. The time required for the elutriation varies from 10 to 24 hours, according to the nature of the clay. When adjusted the device needs practically no attention.

The results of the mechanical analyses of the clays examined are compiled in Table IV.

From the results of the mechanical analysis a numerical value expressing the fineness of grain of the clay as a whole might be calculated. Since the weights of the fractions are known, the average diameters (by microscopic determination) and the specific gravity of the powder may easily be obtained a factor expressing the relative total surface area may be computed, which J. W. Mellor[9]

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[9] J. W. Mellor, Jackson's and Purdy's Surface Factors. Trans. English Ceram. Soc. 9, p. 94-114.

TABLE IV

No. of clay	Residue left on sieves in per cent by weight of dry clay							Sediments left in can, in per cent by weight of dry clay			Per cent by weight carried off by over-flow	Kind and amount of reagent employed per 50 grams of clay
	20 mesh	40 mesh	60 mesh	80 mesh	100 mesh	120 mesh	Total residues on sieves	Can No. 1	Can No. 2	Can No. 3		
1	......	......	......	......	......	......	2.32	0.35	0.39	1.12	95.52	1 c c $\frac{N}{10}$ NaOH
2	Trace	11.75	7.03	4.10	5.30	0.77	28.98	14.74	11.79	3.95	40.57	200 c c $\frac{N}{10}$ $Na_2C_2O_4$
3	......	......	......	......	......	......	Trace	0.02	0.24	0.43	99.31	80 c c $\frac{N}{10}$ NaOH
4	......	......	......	......	......	......	1.17	2.83	8.28	2.01	85.71	500 c c $\frac{N}{10}$ NaOH
5	......	......	......	......	......	......	......	......	......	......	99.00	
6	0.05	0.18	2.93	2.60	5.35	0.85	11.96	13.65	19.07	5.14	50.18	50 c c $\frac{N}{10}$ NaOH
7	0.04	0.06	0.04	0.04	0.04	0.02	0.24	0.21	1.04	0.96	97.31	75 c c $\frac{N}{10}$ NaOH
8	0.61	1.49	1.74	0.63	0.55	0.11	5.13	3.15	34.50	9.72	47.50	100 c c $\frac{N}{10}$ NaOH
9	0.02	0.02	0.04				0.08	0.24	6.34	8.74	84.60	30 c c $\frac{N}{10}$ NaOH
10	......	......	......	......	......	0.02	0.02	0.02	10.90	9.52	79.54	30 c c $\frac{N}{10}$ NaOH
11	0.33	0.66	0.35	0.16	0.27	0.04	1.81	2.28	34.09	10.69	51.13	100 c c $\frac{N}{10}$ NaOH
12	0.64	0.98	1.24	1.10	3.54	0.24	7.74	14.30	23.08	7.06	47.82	180 c c $\frac{N}{10}$ $Na_2C_2O_4$
13	1.54	1.83	2.86	0.96	2.22	0.18	9.59	5.66	8.54	8.24	67.97	
14	0.14	0.28	0.46	0.34	0.46	0.04	1.72	0.98	8.03	9.03	80.24	75 c c $\frac{N}{10}$ NaOH

expresses by the formula:

$$\frac{6}{s}\left(\frac{W_1}{d_1}+\frac{W_2}{d_2}+\frac{W_3}{d_3}+\ .\ .\ .\right).$$

Here s = mean specific gravity of the powder, W_1, W_2, W_3 . . . the weights of the fractions, and d_1, d_2, d_3 the average diameters of the grains in the several fractions.

The greater the surface factor the finer is the material, and hence this value may be used to give a relative approximation which serves sufficiently well for purposes of comparison.

Where the limiting diameters of the fractions are known—i. e., the sizes of the largest and the smallest particles for every separation—the mean integral diameter may be calculated from the formula[10]

$$\sqrt[3]{\frac{(d_1+d_2)\ (d^2_1+d^2_2)}{4}}$$

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[10] Mellor, loc. cit.

in which the limiting diameters are represented by d_1 and d_2. The value of this average diameter may then be substituted in the formula for the surface factor given above.

In all of this work the assumption has been made, necessarily, that all the particles are spherical in shape, which of course is not true. Again, the surface factor thus calculated can make no claim to scientific accuracy, owing to the fact that it is difficult to obtain the average sizes of the grains represented by the various sediments, and practically impossible to determine the mean dimension of the particles carried off by the overflow with any degree of correctness. Owing to the fineness of the material floated off its surface valuation constitutes the greater part of the total surface factor. Furthermore, many of the apparent grains are aggregates of still finer material, and it is almost absurd to speak of an average size for the clayey matter. The material carried off contains practically all of the plastic clay substance and in addition the finest particles of granular matter.

In comparing the clays as to their drying behavior the amount of overflow material expressed in per cent is used as the basis of comparison. Generally speaking, therefore, the statement might be made that clays should dry the more difficultly the finer grained they are, the more matter is washed out of them at the low velocity maintained in the third can of the Schulze elutriating apparatus, assuming that the clay substance is of the same character in all of them. Since the latter assumption, however, is inadmissible, the above generalization holds only in a limited sense, in comparing clays of one kind. Still further modifications are made necessary by the size factor of the granular matter, as has already been pointed out elsewhere.

Similarly, a statement to the effect that clays showing the greatest shrinkage are most difficult to dry can not be accepted without qualification for the same reasons applying to the question of fineness. Granted that the greatest volume shrinkage results in the greatest strain upon the clay structure, the fact remains that clays differ widely in tensile strength and hence in the ability to meet these stresses.

If in spite of these objections an attempt is made to differentiate between the clays as to their relative difficulty of drying, it is evident that such a classification may serve only as a general guide. This approximation was obtained by multiplying the drying shrinkage expressed in terms of the true clay volume by the fraction carried off in the overflow of the Schulze apparatus. From this definition it appears that the higher the numerical value thus obtained the more difficultly should the clay dry other things being equal. The drying factors thus calculated are collected in Table V.

TABLE V

Drying Factors

Clay No.	1	2	3	4	5	6	7
A. Fraction carried off by overflow	0.955	0.406	0.993	0.857	0.990	0.502	0.973
B. Drying shrinkage in per cent of true clay volume	99.80	30.30	60.73	54.80	61.96	60.10	49.00
Factor A×B	95.31	12.30	60.30	46.96	61.38	30.17	47.67

Clay No.	8	9	10	11	12	13	14
A. Fraction carried off by overflow	0.475	0.846	0.795	0.511	0.478	0.680	0.802
B. Drying shrinkage in per cent of true clay volume	41.85	25.80	34.80	49.00	51.09	49.05	42.65
Factor A×B	19.90	20.83	27.67	25.04	24.43	33.35	34.17

(d) **Viscous Condition of Clay Suspensions in Water.**—In previous work[11] the writer has made the attempt to correlate the plastic behavior of different fine-grained clays by determining the tenacity of clay slips, representing various mixtures of clay and water, using a modified Coulomb viscosimeter. He was successful in differentiating several well-known clays in a way which agreed with practical observation. In carrying on these experiments it was fully realized, however, that the comparative results obtained do not express viscosity in its proper physical meaning, but that they represent complex functions, the resultant of which seems to be related to the plastic condition of the material. From practical experience it is known that the more plastic a clay is the more power is required to force it through an auger machine or pug mill. Owing to the fact that we are dealing in this case with suspensions, it is evident that various factors enter into the question such as the viscosity of the water which has dissolved some of the salts contained in the clay, the mechanical resistance of the suspended granular matter, as well as that offered by the flocculent matter to the passage through water, etc. In addition the practical difficulty due to the tendency of the materials to settle must be considered. Owing to the fact that the latter feature is especially annoying, it was decided to make use of an apparatus employing a paddle in place of the disc. Such an instrument was found already on the market in the Stormer viscosimeter, which consists in brief of a vertical shaft to which a paddle is attached and which is driven by means of a simple gearing from a grooved pulley. Motion is imparted to the latter by means of a weight attached to the pulley by a cord. The weight used in these experiments was 200 grams. A revolution counter is connected to the vertical shaft. The method of operating the instrument is very simple. The liquid is poured into a square receptacle, taking care that the same level is maintained for each test. The cup is then raised so that the paddle is immersed and by releasing a brake the weight is caused to descend, thus revolving the pulley and transmitting motion to the paddle shaft. By means of a stop watch indicating one-fifth seconds the time required by the paddle to make 100 revolutions is determined. It is also necessary to obtain the time taken for the same number of revolutions in air, and to deduct this reading from every determination. The resistance offered by water is taken as unity by dividing the time required to make 100 revolutions with the paddle immersed in water into the time required to make the same number of turns in the clay suspension, deducting the air constant from each reading.

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[11] Trans. Am. Ceram. Soc. 10, p. 389.

A brief consideration of the principle of the apparatus will show that owing to the variable speed in the different media the results are not strictly comparable. This together with the variable friction constant of the mechanism itself causes the variations in the experimental results to be quite large. However, for the purpose in view the object of carrying on this work was merely to obtain a rough classification of the clays as to their plastic character under the assumption that the resistance offered by clay suspensions of equal content in solids is a function of their plastic behavior, an assumption, however, for which a general proof has not yet been established. In this connection it was desired to locate by comparison certain of the clays examined which have been found to be especially troublesome in drying.

The preparation of the clays for the test consisted in weighing out a certain quantity of the dried material and of a sufficient amount of water and shaking them by mechanical means, so that the slip became as thick as possible and yet permitted the paddle to revolve. This heavy suspension was diluted gradually, so that the desired concentrations of clay were obtained. In this manner a number of dilutions were made and their relative resistances determined.

The initial clay suspensions were shaken in wide-mouth bottles containing a little shot to facilitate the breaking up of the clay particles. The slip was then shaken through a 20-mesh sieve and poured into the viscosimeter cup.

The results of this work are shown in the diagram of figure 3. In spite of the irregularity of the curves it is at once observed that the clays arrange themselves into three groups. That showing the most rapid increase in resistance or tenacity comprises the plastic clays of the purer type, including, however, one member of the impure clays, the material from Fort Pierre. The latter is of such a highly plastic nature that its presence in this group is not surprising. The second group contains all of the glacial clays which show remarkable similarity in this respect. In the third group the Highland fire clay appears, which, as the sole representative of its class, takes its proper place.

The higher degree of plasticity on the part of the purer clays is made very prominent, and this is due not only to the greater fineness of grain, since two of the glacial clays approach them in this respect, but primarily to the lack of granular matter which, though very fine, is ever present in the impure surface clays.

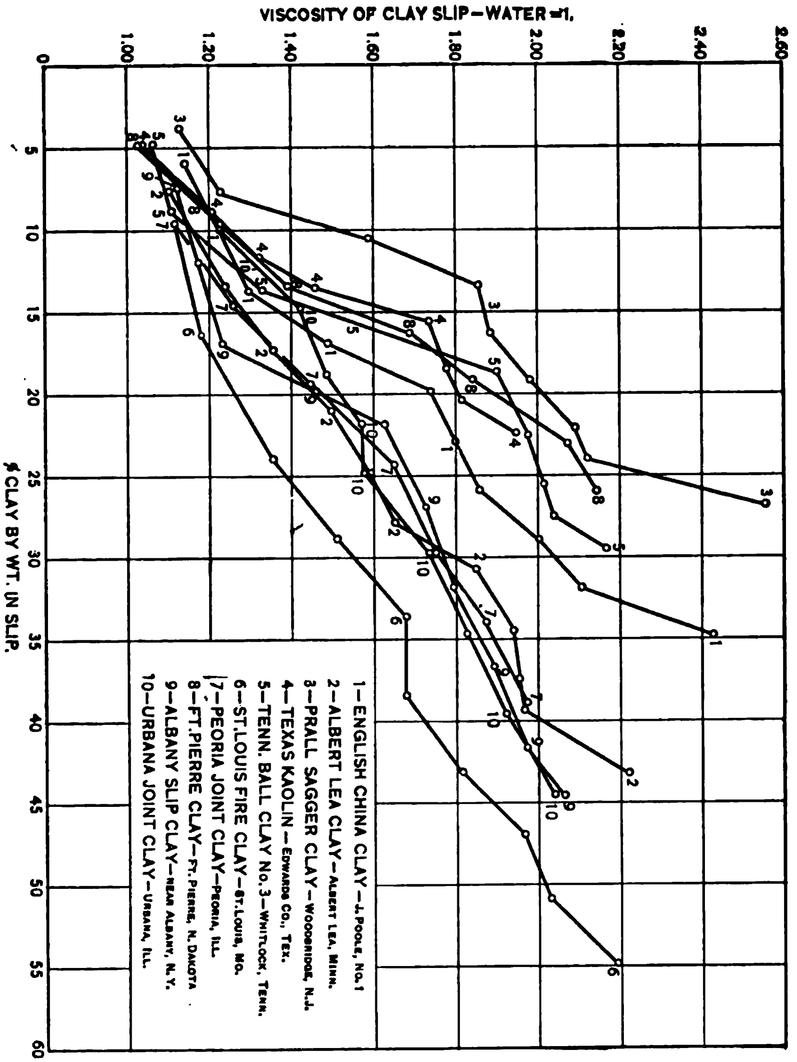


Fig. 3.—*Apparent viscosity of different clay slips with varying contents of clay.*

The latter may reach the highly plastic development of the purer clays, as is shown by the Fort Pierre material, but this is a rare exception. The extreme at the plastic side of the first group is represented by the Prall sagger clay, at the lower end by the English China clay. In this connection the fact must be remembered that all of the clays represent the maximum plastic development, owing to their long-continued stirring in contact with a comparatively large amount of water.

Although this alignment of the clays enables us to obtain an insight into their plastic behavior, we can not draw any deductions as to their difficulty of drying, which, as has been said before, is not necessarily coincident with the highest plasticity. Thus, No. 4, the New Jersey clay, though it is very plastic and possesses high bonding power, offers no decided difficulties in drying, while the joint clays, which are considerably less plastic, become very troublesome in this respect. In considering the subsequent work we must keep clearly in mind, therefore, that a dividing line exists between the pure and impure clays and that any treatment to which both classes are subjected does not necessarily produce the same effect.

5. THE PREHEATING TREATMENT

In studying the effect of heat upon the clays selected for this work it was thought advisable to do this by means of the determination of the volume shrinkages, since the condensation in volume on drying is preeminently the characteristic phenomenon of this process. In practical work clays which dry too difficultly, due to an excessive amount of highly plastic matter, are found to become normal on reducing the shrinkage, for it is evident that the magnitude of the strain to which clays are subjected is a function of the diminution in volume, since it measures the amount of readjustment which must take place.

The objection to making comparisons of the volume shrinkage is that there is no standard consistency of the clay from which to start, so that the amount of water to be used in making up the clays depends upon the judgment of the operator. Various methods for determining the consistency of plastic clay bodies have been proposed, such as the use of the Vicat needle, but none of them give an accuracy greater than that obtained by the "feel" of the clay in manipulating. As has been pointed out before, the proper consistency is fairly sharply defined and any excess or deficiency in water is at once noticed by the expert operator. In the nature of the case, however, slight variations in the water content are unavoidable, especially in working with a material as heterogeneous as clay, of which perfectly uniform samples are difficult to prepare.

In carrying out the preheating experiments a sample of clay sufficient in amount for making all of the test pieces of the series was thoroughly worked and tempered and kept at least 48 hours in a large desiccator containing water, so as to establish conditions of equilibrium. Cylindrical test pieces for the determination of the normal volume shrinkage were then made up and their volume measured as described above. These specimens were then dried to constant weight at 60° C, and finally at 100°. Pats of clay of sufficient size were then removed from the bulk sample in the moist dessicator and dried to the following temperatures in a copper laboratory oven: 150, 200, 250, 300, 350, and 400° C, which were maintained for three hours. The dry pat resulting for each temperature was ground through a 20-mesh sieve and made up with water to its best plastic consistency. In one series of experiments these wet pats were kept over water for 16 hours, in another series for one hour. After this period the moist clay was made up into cylindrical test pieces, the volume of which was found at once. The specimens were then dried and their volume again determined. In addition to the volume both the wet and the dry weights of the test pieces were obtained. During the weighing the specimens were kept in tightly closed tin cylinders.

(a) **Effect upon Drying Shrinkage.**—The specific gravities of the normal as well as of the preheated clays in the powdered condition were carefully determined by means of the pycnometer.

The preheating oven consisted of a cylindrical, air-jacketed vessel of heavy copper, 6 inches in diameter and 5 inches deep inside, the air space being 1 inch. The cover likewise was provided with an air space and had three tubulatures for the insertion of mercury thermometers. The heat was applied by a gas burner and the temperature regulated so that it did not vary on the average more than 5° from the desired point.

In working up the ground, preheated clays into the plastic state it was at once observed that the amount of water required decreased with the increasing temperature treatment, although not in a regular manner, as shown by the curves of Fig. 4, representing seven clays. It appears from the diagram that the drop in the amount of water required is greatest between 200 and 300° with most clays, although there are two exceptions in which this occurs at a higher temperature.

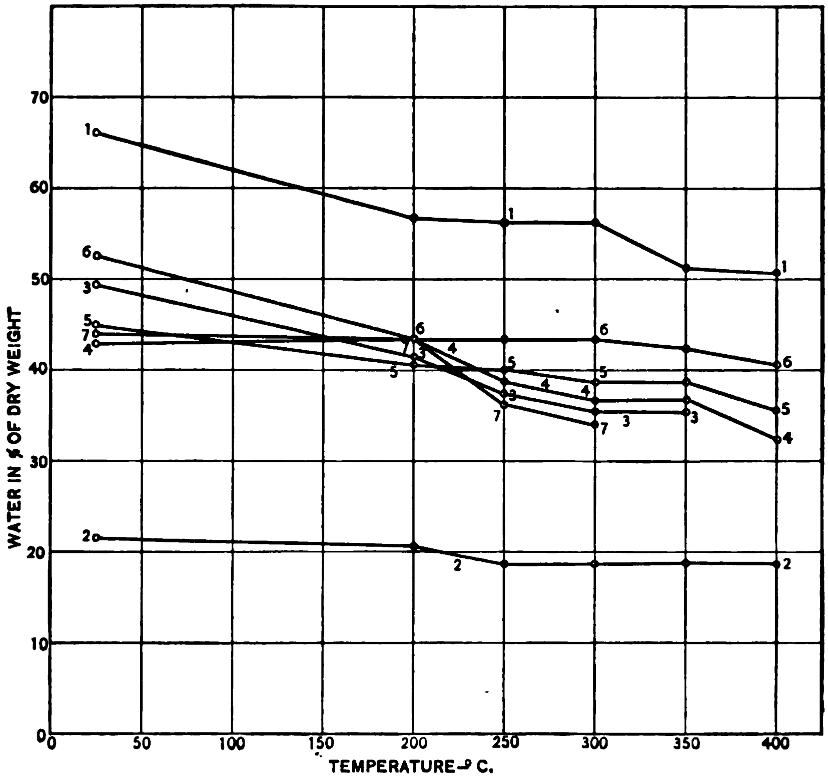


Fig. 4.—*Variation in water content for clays preheated to different temperatures.*

Owing to the fact that, independent of the slight variations in the molding, the amounts of shrinkage and pore water and hence the exterior volumes of the test pieces were not proportionately constant during these experiments, it was decided to express the volume shrinkages in terms of the true clay volume, i. e., the weight of the dried clay divided by its specific gravity, as has been shown before.

The decrease in volume shrinkage thus expressed is shown for the 14 clays examined in Figs. 5 and 6.

The red-burning clays, it is observed, show four types of materials. The first class, represented by No. 1, the excessively plastic material from Fort Pierre, N. Dak., which resembles bentonite in its behavior, evidently stands for abnormal clays, clearly beyond the limits of the workable kinds. It shows an abrupt decrease in the shrinkage curve, beginning at 250°, and continues to lose at a somewhat diminished rate up to the maximum temperature employed. Its final shrinkage still remains so high that no mistake is made by calling this clay hopeless from the standpoint of its commercial use.

In the second class again only one material is represented, No. 13, a reddish-burning clay of the type of the so-called No. 2 fire clays. Its shrinkage loss curve is gradual, being most marked between 350 and 400°. This material being more homogeneous in structure and higher in clay matter than the average red burning clay seems to lose its plasticity more gradually, which differentiates it sharply from the other clays.

The third class of clays includes the average, highly plastic and frequently "sticky" clays of glacial or alluvial origin. The material losing its plasticity most abruptly is from an alluvial deposit. In practically all of them the most significant change took place between 250 and 300°.

In the fourth class we find one fine-grained material of glacial origin, evidently very high in nonplastic matter, which behaves very much like the other clays of the third group, differing only in its low initial shrinkage. It likewise seems to undergo its greatest change between 250 and 300°.

All of the clays, after showing their greatest drop in shrinkage, appear to change in color, assuming a reddish tinge and at the same time become granular. Finally, excepting clay No. 1, they

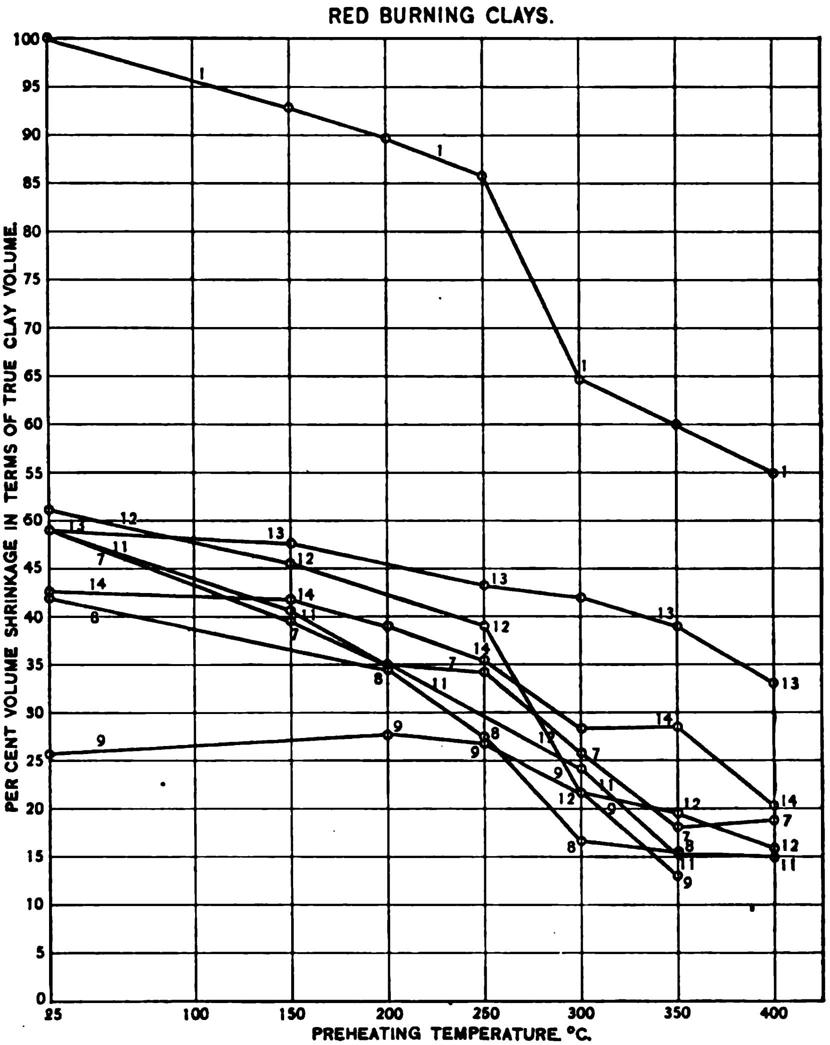


Fig. 5.—*Volume shrinkage of red burning clays, preheated to different temperatures, made again plastic with water and dried at 60° C.*

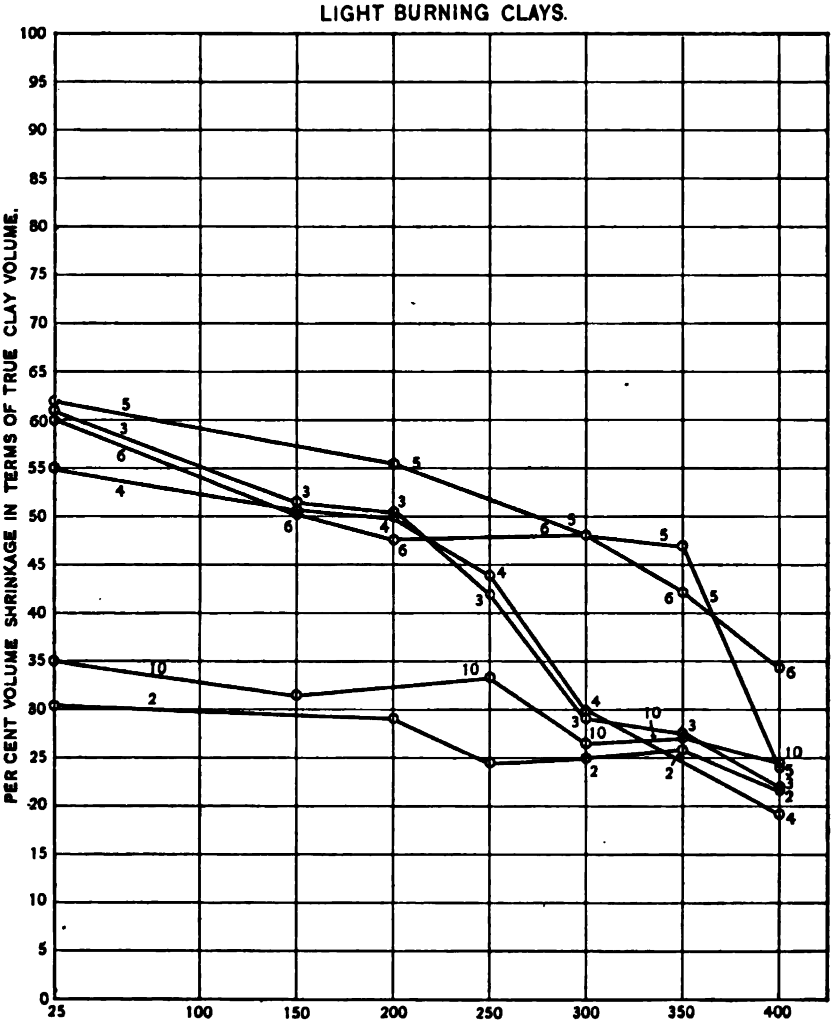


Fig. 6.—*Volume shrinkage of light burning clays, preheated to different temperatures, made again plastic with water and dried at 60° C.*

appear to be sand like and more or less inert in the presence of water. Up to 350° the absorption of water takes place with great eagerness and a sensible amount of heat is evolved.

In the diagram representing the light-burning clays three groups may be recognized:

The first, with only one member, No. 5, an English ball clay, appears to lose plasticity gradually up to a certain point, 350°, when it shows a sudden drop.

In the second group, composed of Nos. 3, 4, and 5, the loss throughout is fairly gradual, although a more abrupt change is clearly observable between 250 and 300°, and in the case of No. 6, at 300°.

The third group evidently comprises the less plastic clays, which with a low initial shrinkage do not appear to have suffered any great changes, although even here No. 10, the English koalin, seems to have been impaired in plasticity at the same temperature as the other clays, 250–300°.

Like the red-burning clays, these materials become granular after the heating treatment and, according to their content of ferric oxide, assume a pink or gray color.

(b) **Rate of Drying.**—From the practical standpoint it seemed important to determine whether preheating had any effect upon the rate of drying. For this purpose eight clays were made up into cylinders of the same initial size and dried in a water-jacketed oven, at a constant temperature of 60°. The specimens were removed every hour and weighed. In every case it was found that the rate of drying of the preheated clays was identical with that of the normal materials, though, of course, the amount of water required to develop plasticity differed in the preheated materials from the normal amount. In Fig. 7 the curves of clay No. 1 are presented which are typical for all of the materials tested and show clearly that preheating does not influence the rapidity of drying.

In order to establish the rate of drying a clay in the raw and the preheated state under conditions permitting only of slow evaporation, a 200-pound sample of so-called swamp clay, very difficult to dry, was used. One-half of the sample was made up into 3.5-inch cubes on a small auger machine in the raw condition.

The other half was preheated to 250° C. before being made up into test pieces of the same dimensions. Of these, three cubes made from the raw and three from the preheated clay were selected and placed in a closet, maintained at room temperature, as close together as possible and their weights determined at intervals. In Fig. 8 the curves representing the loss of water of these specimens are shown, and it is seen that the rate of evaporation of the preheated clay approaches closely that of the raw material.

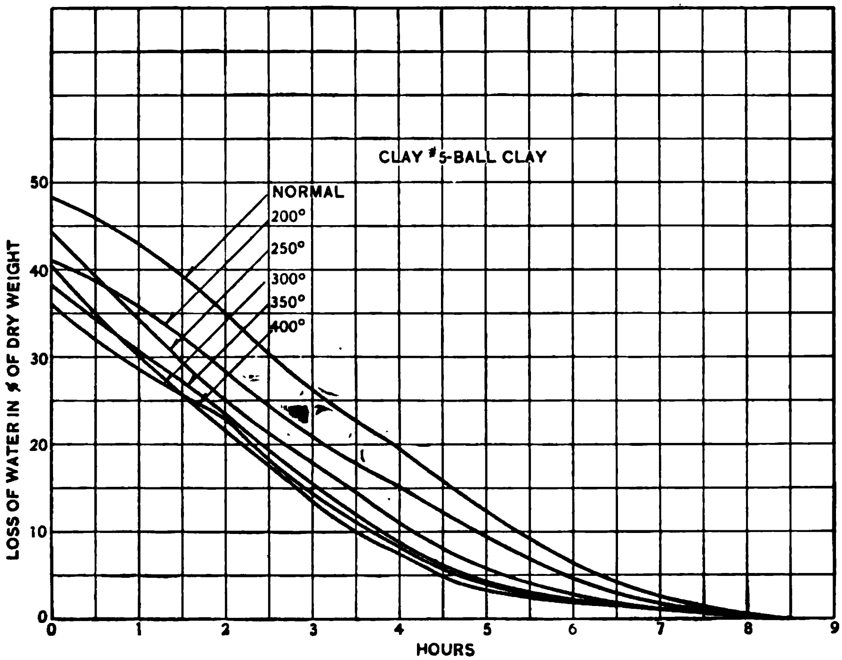


Fig. 7.—*Rate of drying of clay, preheated at different temperatures, again made plastic wtih water and dried at 60° C., compared with rate shown by the untreated clay.*

6. THE PRACTICAL EFFECT OF PREHEATING

In the experiments just described it has already been shown that preheating has decreased the drying shrinkage. From this it might fairly be assumed that clays should dry more easily in the preheated than in the raw condition.

Experimental proof of this fact was obtained by working up batches of about five hundred pounds each of seven clays, both

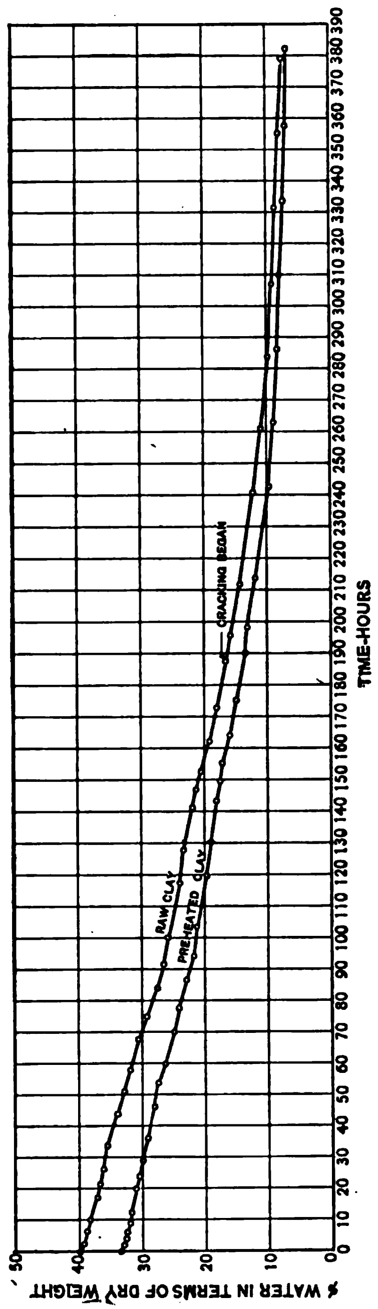
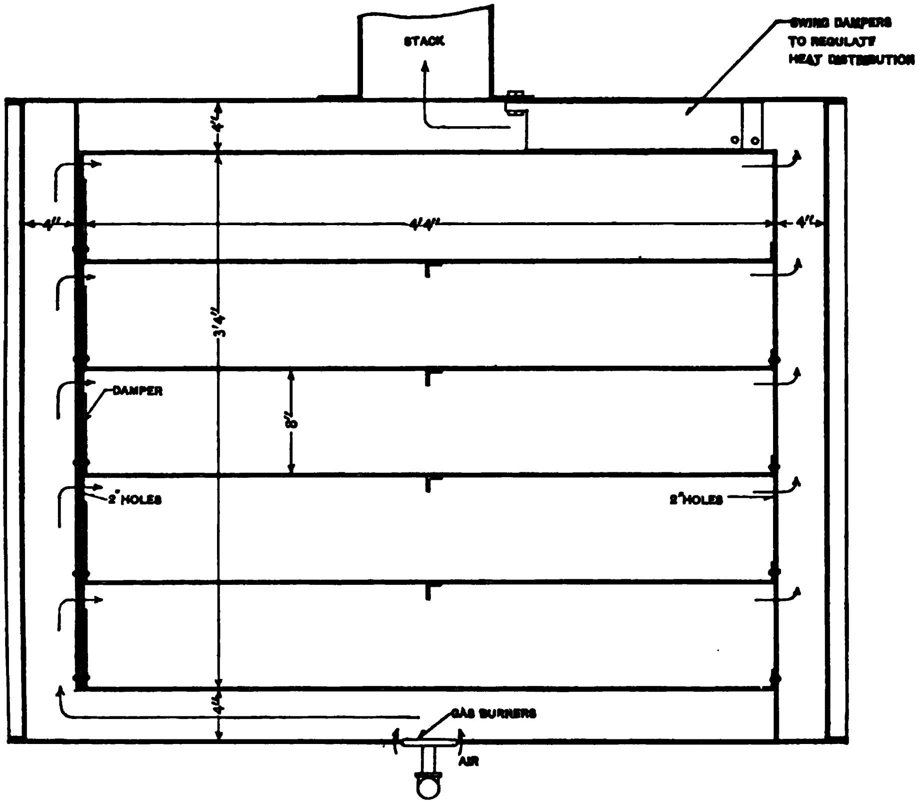


Fig. 8.—Rates of drying of 3½ inch cubes pressed from normal clay and clay preheated at 250° C.

in the raw and in the preheated condition to the plastic state and putting them through an auger machine of commercial size. The clays were of the red burning type as employed in brick making, and were obtained from the following localities: Albert Lea, Minn., Heron Lake, Minn., Urbana, Ill., Peoria, Ill., Groveport, Ohio, Athens, Ohio, and a so-called swamp clay from Curtice, Ohio.



SECTION VIEW OF GAS DRYER

Fig. 9.—*Diagram of gas-fired drying oven used for preheating larger quantities of clay.*

The clay samples were preheated in a specially constructed sheet-iron oven fired with gas (Figs. 9 and 10), in which the heat distribution permitted of close regulation. This is accomplished by carrying the gases under the bottom plate up a collecting space on one side, from which they are distributed to each compartment. The admission of the heated air to each space is regulated by means of a grid sliding damper. At the exit sides of the oven the gases are again collected in a flue of the width of the oven and taken to the top, where they are removed through a central opening into the stack. In the double space on top through which the gases are removed, two hinged dampers are provided for throwing the heat to either side to compensate for the radiation losses on the front and back sides of the oven. Through tubulatures thermometers are inserted for controlling the temperature. After proper damper adjustment was made it was possible to keep the temperature constant within several degrees, assuring an accuracy ample for the purpose of the work. The preheating temperature adopted was 250° C and the time of drying six hours.

The raw clays were tempered in a wet pan, while the preheated materials were ground dry, screened through a piano-wire screen, and then made plastic in the pan. After tempering, the clay was taken to the auger machine (Fig. 11), and pressed through a non-lubricating die into a round column 3½ inches in diameter. The cylindrical bar was cut up into discs 1½ inches thick, which were dried and their volume shrinkage noted. It was found in this connection that while the working behavior of two clays was decidedly improved by preheating, the others showed the need of lubrication, which it was impossible to provide. The result was that the test specimens were produced under conditions of strain.

In drying, it was found that one material, the clay from Heron Lake, Minn., cracked neither in the raw nor the preheated condition. Of the remaining six clays, in every case the discs made from raw clay cracked more or less badly, while those made from the preheated clay did not crack at all. The drying losses are compiled in Table VI. The number of test specimens made varied from 60 to 100, and for this reason the percentages expressing the drying loss are not of equal value.

It was observed especially on two preheated clays, the ones from Peoria and Groveport, that drier efflorescence was quite marked. From this it would appear that preheating releases the soluble salts such as the sulphates of potash, soda, lime, and magnesia contained in the clay, which, on the evaporation of the water, are carried to the surface and give rise to the discoloration

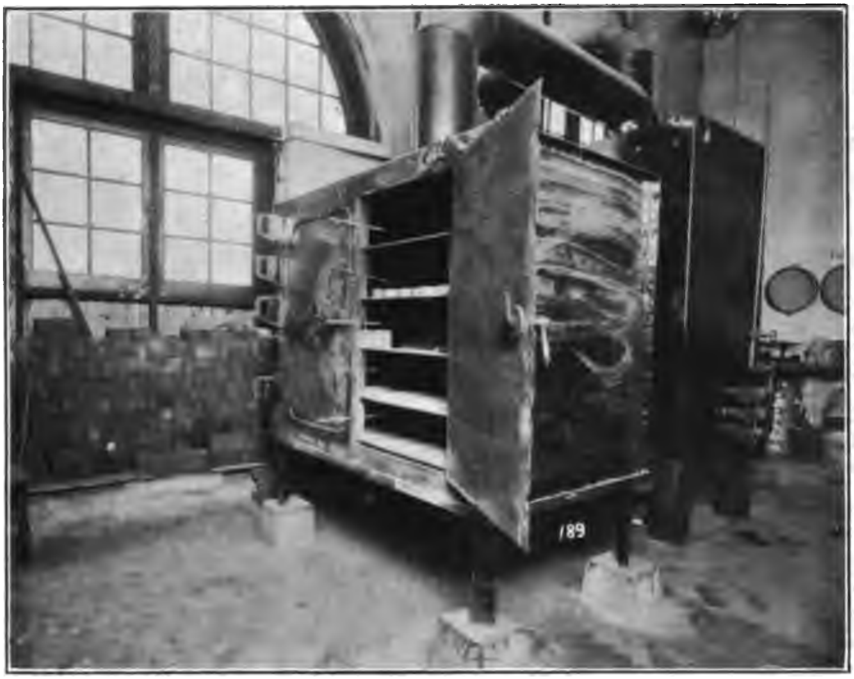


Fig. 10.—*View of Preheating Oven.*

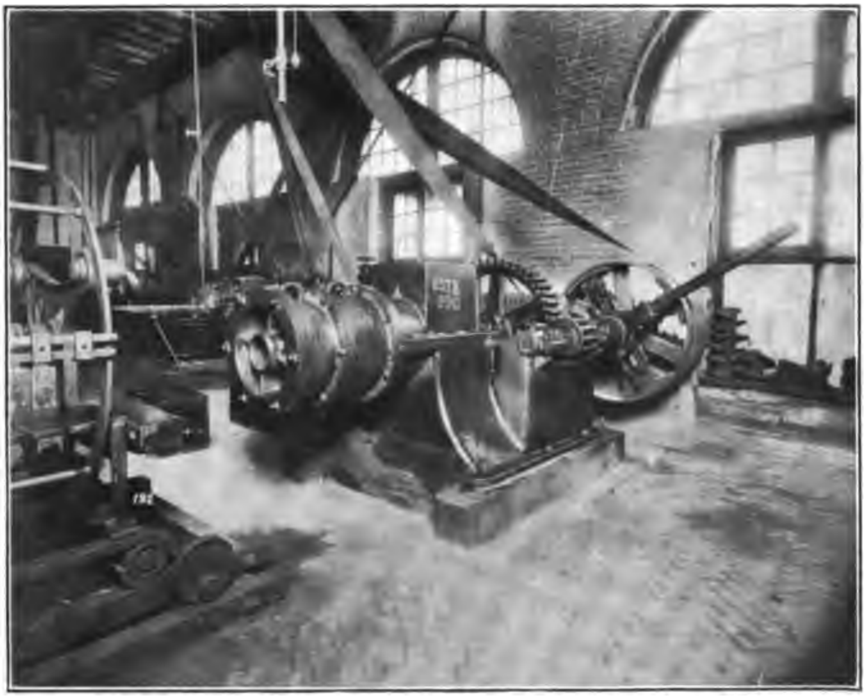


Fig. 11.—*View of Auger Machine.*

commonly known as "white wash." The adsorbing power of clay thus seems to be diminished by this treatment, and in some clays the resulting discoloration might prohibit their use for the manufacture of face brick and similar products. It was evident, however, that this effect varied with the character of the clay, its physical structure, and its content of soluble salts, and hence can not be considered a necessary result in every case.

TABLE VI

Percentage Drying Loss

Clay	Per cent drying loss of test pieces made from raw clay	Per cent drying loss of test pieces made from preheated clay	Remarks
Albert Lea, Minn.	95	0	
Heron Lake, Minn.	0	0	
Urbana, Ill.	90	0	Repeated with clay preheated to 300°
Peoria, Ill.	95	0	Repeated with clay preheated to 300°
Groveport, Ohio	100	0	Repeated with clay preheated to 300°
Athens, Ohio	100	0	
Curtice, Ohio	100	0	

7. THE CAUSE OF THE IMPROVEMENT IN THE DRYING BEHAVIOR DUE TO PREHEATING

It has thus been shown beyond doubt that the drying of excessively plastic clays is facilitated by preheating, that evidently the resistance to the capillary flow has been decreased so that the difference between the amount of water evaporated from the surface per unit time and that supplied from the interior of the clay mass is no longer great enough to cause strains which lead to checking.

There remains now the task of determining the cause of this improved condition.

This part of the problem was attacked by means of the following methods: 1. Determination of the specific gravity of the clays preheated to different temperatures. 2. Mechanical analysis of the normal and preheated clays. 3. Determination of the adsorbing power of normal and preheated clays from malachite green in solution. 4. Determination of the distribution of shrinkage and pore water.

Specific Gravity: In these experiments a pat of plastic consistency weighing about a pound was made up of each clay which was cut up into smaller lumps for preheating at the different temperatures. The preheating was done in the small drying ovens referred to above. The preheated specimens were then crushed and passed through a 60-mesh sieve. By means of the pycnometer the specific gravity of each sample was determined, care having been taken to eliminate the inclosed air by connecting up the specific gravity bottle to a suction pump and heating in warm water up to the boiling point. Ample time was allowed for cooling in running water and the final temperature of the liquid in the pycnometer was taken into account. It was found that the specific gravity of the clays differed even in the same lump, and it proved difficult to bring about the desired homogeneity of the sample. The results of these determinations are given in Table VII. Though the irregularity in the results is evident, it is seen that all but one clay show a noticeable increase in specific gravity due to preheating which must be ascribed in part to the expulsion of the small quantity of hygroscopic water held so persistently and in part to a condensation of the specific volume of the clay. Since it is not likely that the crystalline constituents have suffered any such change at the temperatures involved we must conclude that the effect is confined to the nongranular clay matter. The contraction in volume might be explained by the

TABLE VII

Specific Gravity of Clays

No. Clay	Normal	150°	200°	250°	300°	350°	400°
1	2.451	2.456	2.630	2.603	2.603	2.657	2.621
2	2.537	2.548	2.636	2.612	2.609	2.644	2.647
3	2.577	2.591	2.600	2.600	2.590	2.593	2.590
4	2.596	2.589	2.646	2.629	2.629	2.664	2.664
5	2.560	2.560	2.550	2.605	2.601	2.600	2.600
6	2.510	2.512	2.562	2.545	2.556	2.580	2.573
7	2.510	2.490	2.648	2.638	2.627	2.653	2.665
8	2.603	2.621	2.653	2.650	2.655	2.692	2.696
9	2.784	2.741	2.728	2.725	2.721	2.747	2.751
10	2.476	2.560	2.605	2.639	2.638	2.637	2.644
11	2.575	2.587	2.649	2.650	2.645	2.676	2.697
12	2.680	2.707	2.709	2.729	2.769	2.732	2.696
13	2.768	2.739	2.701	2.761	2.820	2.825	2.773
14	2.645	2.666	2.684	2.712	2.662	2.743	2.708

closing up or shrinkage of the assumed colloidal matter very similar to the contraction of the silicic acid gel and other substances of like character. It is evident that this condensation would involve only the minute, micellean structure of the material and does not refer to the capillary system of the clay aggregate. In making up the preheated clays with water it was observed that some heat was given off. It was thought to be interesting to determine approximately, the amount of heat thus evolved from a normally dried clay and a preheated material. For this purpose a sample of a red plastic surface clay was divided into two parts. One was dried at 105° C, the other was heated to 300°. By placing weighed amounts of the clay into an improvised calorimeter, adding a known amount of water and noting the temperature rise by means of a corrected thermometer reading to 1/50° the heat given off by the clay dried at 105° was found to be almost 4-gram calories and that by the preheated material practically 5 calories per gram.

Mechanical Analysis: In determining the changes brought about by preheating as regards the fineness of grain, four samples of clay were prepared by thoroughly mixing them and dividing each portion into two parts. One half was preheated to 300° C and then put through the Schulze apparatus, the other was run through in the normal condition. The results are compiled in Table VIII. In carrying out this work it became at once evident that the preheated clays showed an extraordinary tendency to form aggregate particles in spite of the fact that they were first mechanically shaken in water and apparently deflocculated by the use of NaOH and $Na_2C_2O_4$ solutions. These particles were found to be so hard that they could not be worked through the sieves by simple rubbing. The results show that for this reason the clays have become decidedly coarser, the surface factor having been decreased. This applies not only to the sieve sizes, but also to the sizes separated by the first two cans. This difference between the normal and the preheated clays appears to be due to coagulation, the fine individual particles forming aggregates of varying sizes. From this it follows that a decided change in the capillary structure of the clay must have been brought about tending either to increase or decrease the pore space. Just in what direction this change proceeds will be shown later.

TABLE VIII

Mechanical Analysis

NORMAL AND PREHEATED CLAYS

Clay	40	60	80	100	120	Cans			Overflow
						1	2	3	
N	0.84	1.77	1.33	3.78	0.20	8.02	15.12	2.21	66.72
G[1]300°	4.04	5.76	2.42	7.08	0.39	16.90	16.28	3.00	44.13
N	1.96	1.80	1.50	3.37	0.16	4.07	4.45	2.32	80.37
A[2]300°	4.56	2.66	1.96	1.33	0.22	5.47	8.38	5.01	70.40
N	1.11	1.37	0.58	0.70	0.15	2.79	26.56	5.07	61.66
S[3]300°	9.54	9.28	3.26	2.20	0.10	5.74	37.25	4.39	28.23
N	0.30	0.40	0.34	0.50	0.08	0.83	3.84	6.18	87.52
H[4]300°	3.71	2.77	0.71	1.99	0.33	3.29	5.57	4.44	77.17

[1] Alluvial clay, Groveport, Ohio. [2] Impure No. 2 fire clay, Athens, Ohio. [3] Joint clay, Urbana, Ill. [4] Glacial clay, Heron Lake, Minn.

Malachite Green Adsorption: H. E. Ashley[12] employs the ability of clays to absorb complex organic salts, such as malachite green, from their solutions as a means of comparing the plasticity of different clays, and makes the assumption that, other things being equal, the more plastic a clay the more of the dissolved substance it takes out of solution. In casting about for a numerical factor expressing the plasticity of a clay, however, he found it necessary to introduce two modifying factors, drying shrinkage and fineness of grain, as expressed by the Jackson-Purdy surface factor. He thus arrives at the expression:

$$P = \frac{C\,B}{A}, \text{ where—}$$

P = numerical value proportional to plasticity.

C = relative colloid content, based upon the amount of organic salt (malachite green) absorbed.

B = per cent shrinkage of clay discs made by casting the lawned slip into plaster molds.

A = surface factor.

Ashley hence assumes that plasticity is proportional to the amount of malachite green adsorbed from solution and to the drying shrinkage and inversely proportional to the fineness.

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[12] Bulletin 388, United States Geological Survey.

Since in connection with the present work the fact that plasticity has been decreased by the preheating treatment has been established beyond doubt, it was thought to be of interest to determine the differences in the absorption of malachite green by preheated clays. This work was done by Mr. H. E. Ashley, and consisted in shaking one gram of clay by mechanical means in 100 cc of a malachite green solution containing 0.3 gram of the dye. The amount of malachite green remaining in solution was determined colorimetrically. The value thus obtained was then expressed as the relative adsorption capacity of the different materials in terms of the adsorption shown by a standard plastic clay, the Tennessee No. 3 ball clay. The latter was assumed, therefore, to show a colloidal value of 100. A clay giving a value of 75 should then contain 75 per cent of the colloid matter present in the Tennessee clay. The results of these determinations are compiled in Table IX.

TABLE IX

Adsorption Factors of Normal and Preheated Clays

Clay	Surface clay, Albert Lea, Minn.	Joint clay, Urbana, Ill.	Joint clay, Peoria, Ill.	Alluvial clay, Groveport, Ohio	Impure No. 2 fire clay, Athens, Ohio
Normal................	600	142	175	104	160
Preheated at 250° C....	475	137	150	106	140

Inspection of these figures shows at once that, although in four out of the five cases the adsorption has been decreased, the difference is not in proportion to the difference in the physical behavior of the clays. It is evident, therefore, that, with the exception of the Minnesota clay, no decided change in structure is indicated by these tests. It would seem then that the partially irreversibly "set" gel shows the same adsorption as the reversible gel, and that the adsorption of malachite green, from its solution, does not appear to be any measure of plasticity, as far as these preheated clays are concerned.

Distribution of Shrinkage and Pore Water.—From the results of the mechanical analyses of the normal and preheated clays, as well as from direct observation made during the course of the shrinkage experiments, it became evident that the amount of pore water in the preheated clays differed from that present in the normal materials. It hence was found necessary to determine the amounts of shrinkage and pore water present in the same clay after heating it to different temperatures. This was done similarly to the previous calculations of the drying shrinkage expressed in terms of the true clay volume. These results are collected in Table X.

TABLE X

Distribution of Shrinkage and Pore Water

Clay		Per cent by volume in terms of true clay volume.						
		Normal	150° C	200° C	250° C	300° C	350° C	400° C
Alluvial clay, Groveport, Ohio, No. 12.	Total water........	87.20	80.52	71.11	73.00	72.60	74.60	70.80
	Shrinkage water..	51.09	45.49	37.61	39.22	21.70	19.66	15.98
	Pore water........	36.11	35.03	33.50	33.78	50.90	54.94	54.82
Glacial surface clay, Heron Lake, Minn., No. 13.	Total water........	95.20	90.00	92.60	90.70	84.30	97.10	84.40
	Shrinkage water..	42.65	41.80	38.92	35.37	28.27	31.17	20.35
	Pore water........	52.55	48.20	53.68	55.33	56.03	65.93	64.05
Impure No. 2 fire clay, Athens, Ohio, No. 14.	Total water........	72.19	78.06	73.17	70.33	75.78	71.60	71.88
	Shrinkage water..	49.05	47.55	47.43	43.23	49.06	38.96	33.34
	Pore water........	23.14	30.51	25.74	27.10	33:82	32.64	38.54

For the sake of facilitating comparison the relations obtained are shown graphically in Figs. 12, 13, and 14.

Referring to Fig. 12, it is observed that with this clay a marked increase in the amount of pore water is shown between 250° and 300°, and it is quite evident that the clay approaches the condition of an inert, nonplastic material as the shrinkage water decreases. The two curves will meet at the point at which the clay will have lost its plasticity. This increase in pore space shown brings out the fact that the preheating of clays causes them to become more porous, and it offers the explanation of the improved drying qualities of the materials thus tested. The increased pore space opens up the clay body, reduces the surface tension, and thus offers less resistance to the flow of water through the capillary system toward the end of the shrinkage when drying conditions are most severe. Owing to the smaller shrinkage it

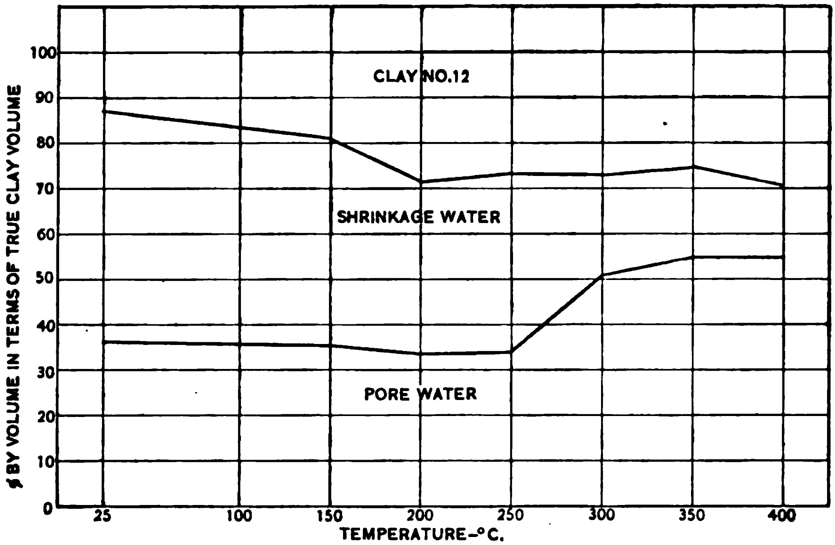

Fig. 12.—*Relation of shrinkage to pore water of Groveport, O., clay preheated at different temperatures, again made plastic with water and dried at 60° C.*

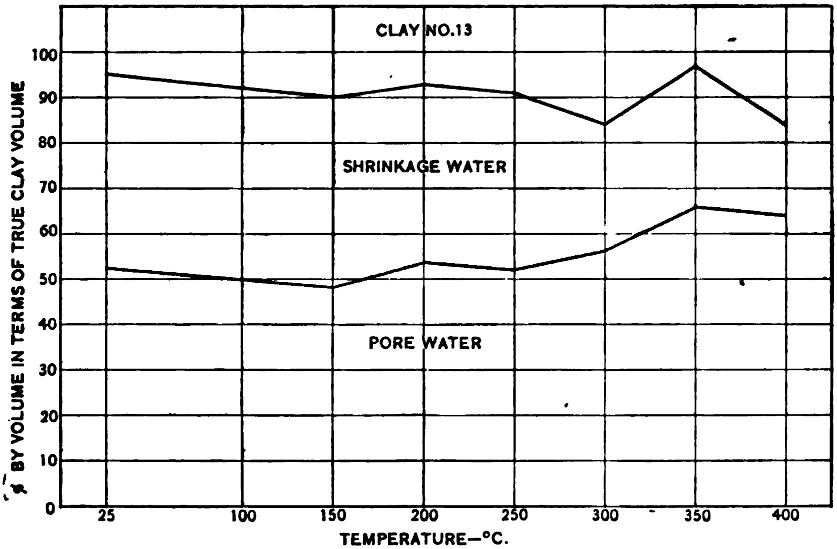

Fig. 13.—*Relation of shrinkage to pore water of Heron Lake, Minn., clay preheated at different temperatures, again made plastic with water and dried at 60° C.*

is evident that the total strain due to contraction is lessened. As has been shown above, however, the actual rate of evaporation from, for instance, two cubes of the same initial size, one consisting of raw and the other of preheated clay under the same conditions of temperature and humidity are about the same. This comparison is not quite fair, since the preheated clay cube would contain somewhat more weight of material than the other.

The clay represented by Fig. 13—a plastic, impure glacial clay—showed likewise a constant increase in the amount of pore water at the expense of the shrinkage water, but the change appears to be more gradual. The shrinkage water retained by the clay heated to 400° still constitutes a large part of the total water, thus indicating that the residual plasticity is still considerable. This clay should be a safe material for preheating purposes.

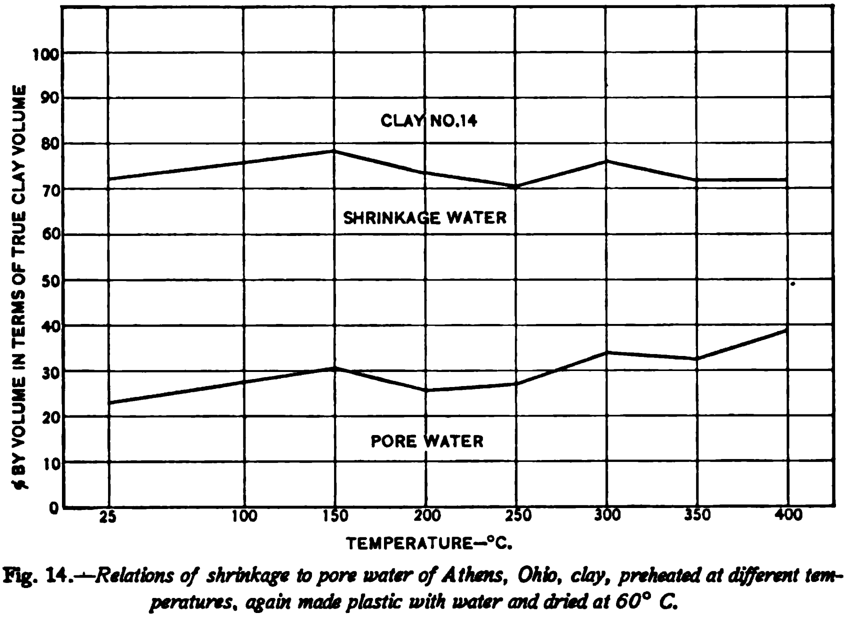

Fig. 14.—*Relations of shrinkage to pore water of Athens, Ohio, clay, preheated at different temperatures, again made plastic with water and dried at 60° C.*

In Fig. 14 the material, a fire clay, shows a decrease in shrinkage water between 300°–400° and a fairly high amount of shrinkage water at the highest temperature. It is evident that if preheating were necessary in this case the temperature could exceed 300°.

From these illustrations it appears that the proper preheating temperature varies for different clays. While in certain materials the desired change to a more nonplastic condition is brought about gradually it is abrupt in others. It is evident from this consideration that the permissible temperature range in the former case is considerably wider than for the latter, where an excessive temperature might carry the conditions too close to the inert state.

From the work done in the present study no general conclusions can be stated as to the behavior of all kinds of clay. As a broad proposition, it might be said that the more impure clays show as a rule a more abrupt change and more narrow temperature limits than the more homogeneous plastic clays of the No. 2 fire-clay or ball-clay types.

In regard to the time required for the preheating no attempt has been made to look into this matter, but it would appear from the present work that it is simply a question of transmitting the heat through the lumps of clay. The larger the average size of the clay lumps the longer should be the time allowed for the heating. From this it follows that it would be policy in commercial work to shred or cut up the material before introducing it into the drying apparatus. Under the conditions of practice the temperature of the rotary dryer is best maintained close to 500° C, and the time of passage through the dryer reduced accordingly.

8. THE EFFECT OF PREHEATING UPON THE MANUFACTURE OF CLAY PRODUCTS

Since it has been shown by experiment that the pore space of preheated clays increases as the clay particles gradually assume the character of more or less inert, sand-like matter, the question arises whether it might not be possible that some clays, even though preheated at lower temperatures, would become too porous to be worked successfully by certain molding machines used in practice, due to the fact that the permissible limit of pore water had been reached. Under this condition might it not be that owing to the greater average distance between the particles the cohesive force would not suffice to hold the mass together if a larger amount of water is used than is necessary to bring the clay to the condition in which it is used in auger machines?

This point was investigated by making up two preheated surface clays with a large amount of water to the consistency of the so-called "soft-mud" process and making them into bricks in regular wooden brick molds. It was found in both cases that the clays showed a decided tendency to "slump" and that they were too weak to withstand the drying strains, resulting in bad cracking and checking. The same preheated clays when worked on the auger machine dried without difficulty. This shows that the amount of water used in bringing such a clay to the plastic state must not be excessive. From this standpoint the auger-machine and dry-press process are to be preferred to the "soft-mud" method of molding.

In tempering preheated clay the point of proper stiff plastic consistency is defined more sharply than with the normal material. When the predried clay is worked in the auger machine it is important to provide the best lubrication it is possible to secure, in order that, owing to the decreased plasticity no strains are produced due to the flow of the clay through the die. The tendency to show auger lamination seems to be reduced by the preheating of the clay. Owing to the decreased drying shrinkage, the die or mold may be made smaller where common brick or other porous ware is to be produced. For vitrified products the gain due to the smaller mold size is slight, since, owing to the increased porosity of the dry clay, the burning shrinkage will be greater.

With reference to the burning of preheated clays it has been found that the combined drying and burning shrinkage, the burning being carried through vitrification, is less than in the case of the normal material. Clays differ in this respect, however. While in one instance the difference in the total volume shrinkages was but 1 per cent, in others it was very much greater. In one case the difference amounted to 12.4 per cent, expressed in terms of the dry volume.[13]

For products to be vitrified the factor of the greater porosity in the dried condition may enter into consideration. Since in vitrification the pore space is more or less gradually closed up, due to the softening of the clay, it is evident that the contraction in the apparent volume of a piece of clay ware must be practically equivalent to the pore space of the dried material. The extent to which such a volume shrinkage may take place without injury to the structure, distortion, etc., is evidently limited. While, for instance, a brick made from shale, with an initial compact, dense structure may be vitrified without an excessive contraction during burning, a plastic surface clay, of loose structure on being carried to vitrification will suffer a far greater shrinkage, and hence is much more subject to defects brought about by the contraction in volume. If this clay were now to be preheated at a temperature at which its pore-water content is increased decidedly, it is clear that the difficulty referred to would be accentuated. For instance, referring to Fig. 12, it is reasonable to suppose that this clay when preheated to 300° would likely be troublesome in burning it to vitrification. On the other hand, the clay represented by Fig. 14, under the same conditions, would in all probability behave very similarly to its condition in the normal state.

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[13] A. V. Bleininger and F. E. Layman, Trans. Am. Ceramic Society, 11, pp. 354-365.

From this it follows that some plastic clays, while they may be corrected as to drying behavior by preheating, might crack or check in burning, due to excessive burning shrinkage. The effect of the preliminary drying thus must be determined for each clay, and in any case the preheating must be carried on at the lowest temperature which suffices to overcome the drying defects. In some cases the admixture of normal and preheated clay might be satisfactory.

In practice the preliminary drying is undoubtedly carried on most efficiently in rotary dryers, such as are now in common use in the Portland-cement industry. The cost of the treatment in well-constructed dryers of this type is estimated to vary from 10 to 15 cents per ton of bank clay under the conditions obtaining in the Middle West, including labor and depreciation. This extra cost no doubt is a burden which should not be assumed where the clay can possibly be made to dry satisfactorily by other means, such as the addition of sand, weathering, etc. But where no other material is available and clay products are in demand, owing to lack of timber and stone, or where, as has been found in the case of an Illinois joint clay,[13] even the addition of sand does not overcome the tendency to crack in drying, the treatment offers a possible solution of the difficulty. Five instances are at present known to the writer in which preheating has been found to be the means of overcoming the poor working and drying qualities of certain clays, as has been proved by tests on a large scale.

At the same time it must be remembered that the dry clay can be disintegrated and screened more readily than the clay coming wet from the bank, thus enabling the manufacturer to remove the impurities, such as gravel, limestone, pebbles, and other mineral detritus, which are especially liable to be present in the glacial clays, more cheaply and thoroughly, besides making the operator independent of weather conditions. Also, it is thus possible to produce wares of a higher grade from low-grade material and in districts where other clays are lacking.

9. SUMMARY

The plasticity of clays is decreased by heating at temperatures above 100° C. This change becomes more marked with higher temperatures and is accompanied by reduction of the drying shrinkage upon reworking. According to the nature of the clay, the change proceeds abruptly after reaching a certain temperature or is more or less gradual throughout. A decided alteration seems to occur in most clays between 200° and 300° C, as is shown by the granular appearance of the clay and the decrease in the drying shrinkage. The color also becomes darker, and in ferruginous materials assumes a reddish hue.

The purer clays seem to be affected more gradually by this heat treatment.

The rate of drying of the preheated clays does not seem to differ from the rate for the undried clays.

Excessively plastic clays, which dry difficultly and result in loss due to checking and cracking, behave normally in drying after being preheated. The best temperature for this treatment must be determined for each clay, and invariably the lowest possible temperature giving the desired result should be adopted. Some preheated clays seem to release their soluble salts more easily than the normal materials. Such clays are likely to show dryer efflorescence.

Clays thus treated should be tempered with as little water as possible and require good lubrication.

The cause of the improved drying quality of the preheated clays is to be sought in the increased porosity. It appears that coagulation of the flocculent portion and the fine, nongranular particles of the clay takes place, analogous to the set of certain gels.

The combined drying and burning shrinkage of preheated clays (burnt through vitrification) is less than that of the normal materials. In most cases the drying shrinkage is decreased at the expense of the burning shrinkage, which becomes greater than the normal contraction. In some clays the increased porosity in the dried state may cause the burning shrinkage (if carried through vitrification) to be excessive, in which case the product will show checking or cracking in burning. Such clays, unless their objectionable features in drying can be eliminated by preheating at a low temperature, are not benefited by this treatment.

Preheating offers a possible commercial method for the treatment of excessively plastic clays which can not be worked and dried successfully by other means, subject to the limitations outlined above.

WASHINGTON, December 6, 1910.

THE REFLECTING POWER OF VARIOUS METALS

By W. W. Coblentz

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INTRODUCTION

The present observations are the result of an attempt to obtain a more thorough knowledge of the optical properties of the metals used in incandescent lamps. Several other elements on the border line between the metals and nonmetals, not heretofore examined, are included, since the data are of general interest.

In a paper on the radiation constants of metals[1] attention was called to the fact that all the pure metals thus far examined have the common property of a low reflecting power in the ultra-violet and in the visible spectrum, which rises more or less abruptly to very high values beyond 2μ in the infra-red, and that it was therefore not unreasonable to assume that the unexamined metals, such as tungsten and osmium, have this same property. This follows from the fact that all the members of a group of chemically related substances have similar physical properties. As will be noticed on a subsequent page, this assumption of a low reflectivity in the visible spectrum has been verified to a degree far beyond expectation.

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[1] This Bulletin **5**, p. 339; 1908. So also this Bulletin, **2**, p. 470; 1907, for illustration of the reflectivities of various metals.

Since the reflectivity of metals is a smooth and continuous function of the wave length in the infra-red, there is reason for expecting the reflectivity curves of these heretofore unexamined metals (tungsten, tantalum, etc.) also to be smooth and continuous. Their spectral energy curves must therefore be smooth and continuous in the infra-red (no indentations or protuberances), and experimental curves showing such indentations are to be regarded with suspicion as to the accuracy of the observations.

It is difficult to show experimentally this selective emission in other than colored metals (e. g., gold and copper) by means of emission spectra, and since the emissivity in the short wave lengths appears to have only a small temperature coefficient it is possible to gain some knowledge of the emissivity of the metal at high temperatures by determining its reflectivity at low temperatures. That it is permissible to apply data obtained at low temperatures to the same substance operated at high temperatures follows from the recent work of Hagen and Rubens,[2] in which it is shown that for wave lengths less than 4μ the optical constants of metals vary but slightly, if at all, with change in temperature, which is the region of the spectrum of interest on the question of the selective emission of incandescent lamps with metal filaments. We have therefore a positive qualitative proof of the much discussed and much overworked application of "selective emission" (combined with a high operating temperature) to explain the high luminous efficiency of metal filament lamps. As will be noticed in the appended illustrations, the selective emission must lie in the visible spectrum. Here the emissivity is almost 50% (for tungsten) while in the infra-red it is only from 4 to 10% that of an ideal radiator, or "black body."

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[2] Hagen & Rubens, Phys. Zs., **11**, p. 139, 1910; Verh. Phys. Gesell., **10**, p. 710; 1908.

In the present experiments a fluorite prism, a mirror spectrometer, and a new vacuum bolometer were used. The unknown metal was compared with a new silvered glass mirror of which the reflecting power is known. The absolute value of the reflectivity of the unknown metal was obtained by multiplying the observed reflectivity by the reflectivity of silver given in Table II (data from Hagen and Rubens).

A Nernst glower was used as a source of radiation, which permitted making observations in the extreme blue and at 10μ where the fluorite prism is almost opaque. Since the glower is very narrow it is necessary to have a very accurate adjustment of its images, reflected from the two mirrors upon the spectrometer slit, so as to avoid a systematic error in the reflectivity. The observations in the infra-red were further verified by using a Nernst "heater" instead of the glower.

In the blue and beyond 8μ in the infra-red the accuracy is of the order of 2 to 3%, while in the intervening region the accuracy is of the order of 1 per cent. There is no difficulty in obtaining high accuracy since we are concerned only with ratios of two numbers (galvanometer readings) which are of nearly the same value, and which are subject to the same errors of observation. In view of the physical nature of the material, and especially of the size of the specimens obtainable, and also of the indirect comparison with silver, it would be illusory to attempt to attain a higher accuracy for the absolute values. This is especially true of tungsten and molybdenum in which the mirror surface was ground upon one face of a rectangular prism of the pure metal 20 x 6 x 6 mm on an edge, kindly prepared for us by the General Electric Company. The narrowness of the specimen does not permit the grinding and polishing of an optically plane surface. The dimensions of the tantalum mirror were 15 x 10 x 1 mm; it was prepared by Siemens and Halske and was optically plane and highly polished. The close agreement between the observed reflectivity of tungsten and molybdenum at 12μ and the theoretical value obtained from a knowledge of the electrical conductivity is therefore to be regarded as somewhat accidental. The angle of incidence of the light upon the mirrors was from 12 to 15 degrees, which is sufficiently small to be considered normal incidence, and hence the loss by absorption (100-reflectivity) is a measure of the emissivity of the metal.

From his observations on the optical constants (the refractive index *n*, and extinction coefficient *k*), at 0.579μ Wartenberg[3] computed the reflecting power of various metals, some of which are included in the present paper. It will be noticed in Table I that the results obtained by the two methods are in excellent agreement in all samples having a good polish.

TABLE I

Substance	Reflecting Power	Substance	Reflecting Power
Manganese	63.5 p. c.	Tungsten	48.6; *51
Chromium	69.7; *55	Palladium	65.0
Vanadium	57.5; *57.5	Rhodium	78.3; *77.5
Tantalum	43.8; *45	Platinum	72.5
Niobium	41.3	Iridium	74.6; *75
Graphite	22.3; *23	Silicon	35.7; *32

*Observations by W. W. C.

It will be noticed that even in the visible spectrum the same magnitude of the reflectivity is to be found within a group of metals. For example, in the platinum group the reflectivity does not fall below 70 per cent, while in the chromiun group the reflectivity centers about the 60 per cent point. However, only beyond 12μ is this relationship true in general.

TUNGSTEN

The area of the mirror examined was 5 mm x 17 mm. This specimen was made from the pure material, which is somewhat brittle and did not permit a polished surface perfectly free from pores, except in the center. This causes a slight scattering for wave lengths up to 3μ (see discussion under graphite).

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[3] Wartenberg, Verh. Deutsch. Phys. Gesell., 12, p. 105; 1910. Hennig. Zeit. Instk. 30, 61, 1910; gives similar data on the reflectivity observed by direct measurement.

TABLE II

Wave length in μ=.001 mm	Reflecting Power													
	Silver	Platinum	Rhodium	Tungsten	Molybdenum	Iron	Tantalum (Wartenberg's sample)	Chromium	Vanadium	Antimony	Silicon	Magnesium	Tellurium	Graphite
.40μ	84.0	48	......	47.0	44.0	......	......	......	......	......	......	......	......	21
.46	89.0	55	......	48.2	44.6	......	......	......	......	......	......	......	......	22
.5	90.0	58.4	76	49.3	45.5	55.0	38.0	55	57.0	......	34	72.0	......	22.5
.6	92.5	64.2	......	51.3	47.6	57.5	45	......	......	53	32	73.0	49	23.5
.7	94.2	69.0	79	54.0	49.8	59.5	56	56	58.5	......	30	......	......	24.0
.8	95.1	70.3	81	56.3	52.3	61.5	64.5	......	59.5	......	29.2	......	48	25.0
1.0	96.4	73.0	84	62.3	58.2	65.0	78.5	57	61.3	55	28	74.0	49.5	26.8
1.2	97.2	75.0	86.5	68.2	63.6	68.5	84	......	63	......	......	......	50	28.3
1.4	97.6	76.8	88.3	73.8	69.0	71.5	86.5	59	64.5	......	28	75	.....	30.0
1.6	97.8	78.0	89.5	78.0	74.2	74.3	88	61	66	58	......	......	51	32.0
2.0	97.9	80.6	91	84.6	81.6	78.0	90.5	63	69	60	28	77	52	35:2
2.5	97.9	......	91.6	89.2	85.5	81.5	91.6	66	71.7	......	......	79	53	39.5
3.0	98.0	88.8	92	90.5	87.6	84.5	92.3	70	74.3	65	28	80.5	54	43.0
3.5	98.3	......	......	92.0	89.2	87.5	92.8	......	76.7	......	......	......	55	46.0
4.0	98.4	91.5	92.5	92.8	90.5	89.5	93.0	76	78.8	68	28	83.5	57	47.5
5.0	98.5	93.5	93	94.0	92.0	91.5	93.0	81	82	......	......	86	60	50.5
6.0	98.6	......	93.5	94.6	93.0	93.0	......	85	85	70	28	88	63	52.0
7.0	98.6	95.5	93.5	95.1	93.3	94.0	93.5	......	87.8	......	......	91	68	53.5
8.0	98.8	95.1	94	95.6	93.7	94.0	93.8	89	89.8	......	......	93	72	55.5
9.0	98.9	95.4	94.5	95.5	94.0	93.8	......	92	92	72	28	93	78	57.5
10.0	99.0	95.9	......	95.5	94.5	......	......	93	......	......	......	......	......	59.0
12.0	98.9	96.5	......	96.3	95.2	......	95.0	......	......	......	......	......	......	......
12.0 μ	......	......	......	*97.2	*97.3	......	*95.3	*97	......	......	......	......	......	......

* Values computed from the electrical conductivity.

In Fig. 1 and in Table II it will be noticed that the reflectivity of tungsten rises abruptly from a low value of 50 per cent in the yellow to 89 per cent at 2.5μ, beyond which point it increases gradually to 96 per cent at 10μ. This is a characteristic of pure metals.

Hagen and Rubens[4] have shown that for long waves (greater than 12μ) the absorption (100-reflectivity) of a metal may be computed from its electrical conductivity by means of the formula $100 - R = \frac{36.5}{\sqrt{c\lambda}}$, where R is the observed reflecting power, c is the reciprocal of the resistance, in ohms, of a conductor 1 m long and 1 sq. mm in cross section, and λ = wave length in μ = .001 mm.

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[4] Hagen & Rubens, Ann. der Phys. (4) **11**, p. 873; 1903. Coblentz, this Bulletin, **2**, p. 470; 1907.

The specific resistance of a squirted rod (hence probably not so pure as the mirror material) of tungsten 20 cm long and 1.2 mm in diameter was determined by Mr. J. H. Dellinger to be 0.000 006 9 ohm per centimeter cube at 21°.8 or 3.99 times that of copper. The sample of tungsten upon which the reflectivity oberservations were made had a specific resistance of 0.000 006 3 at 21°.5 C, or 3.66 times that of copper. Its density was 10 (true value about 19 or 20), which indicates that there were hollow spaces along the axis of prism of metal, which was about 2.5 cm long and had been broken from a longer rod. At one end of this specimen there was a small cavity, but it was not possible to tell how far it extended along the central axis of the specimen. This would cause a higher resistance than the true value. Recent determinations by Fink and by Parani indicate a specific resistance of about 0.000,005 for annealed tungsten. From the specific resistance of this sample of tungsten the computed reflectivity, from the aforesaid formula, using $\lambda = 12\mu$, is 97.3 per cent, while the value obtained by extrapolating from 10μ is 96.3 per cent. As already stated, this is in closer agreement than is to be expected from the observations and from the size of the mirror employed. It may be noticed in Table II that the infra-red reflectivity of tungsten is the same as that of platinum, and in the visible it is the same as that of steel.

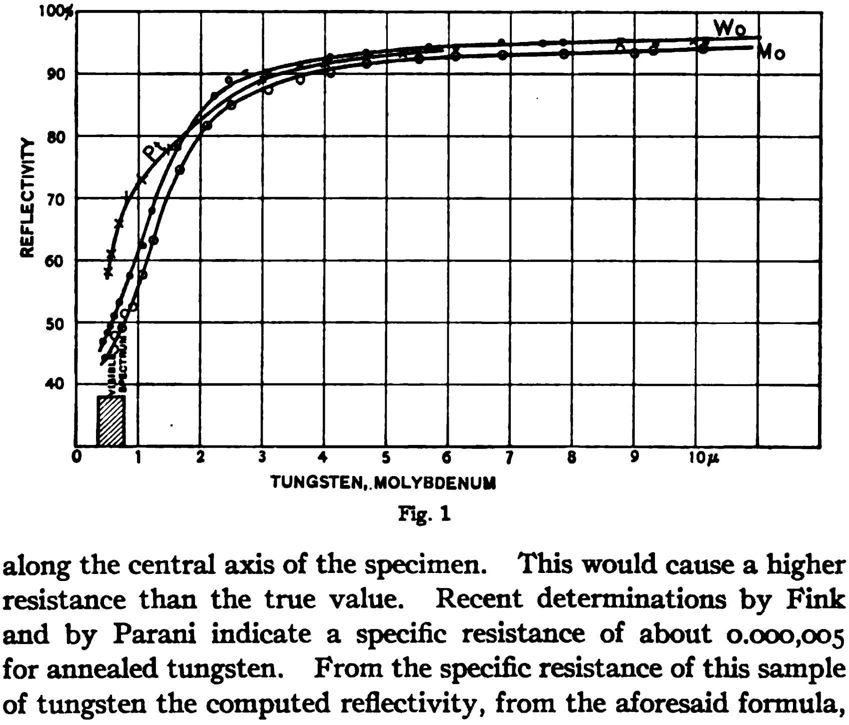

Fig. 1

For a perfectly polished surface, free from pores, the reflectivity of tungsten would be somewhat higher out to 2μ, because of the elimination of the diffuse reflection which obtained in the present sample. (See graphite, which gives an extreme case of diffuse reflectivity.) The results show that in the previous investigation of the radiation constants of metals, it was permissible to assume that the same emissivity function obtains as in platinum, with, of course, different numerical values of the constants.

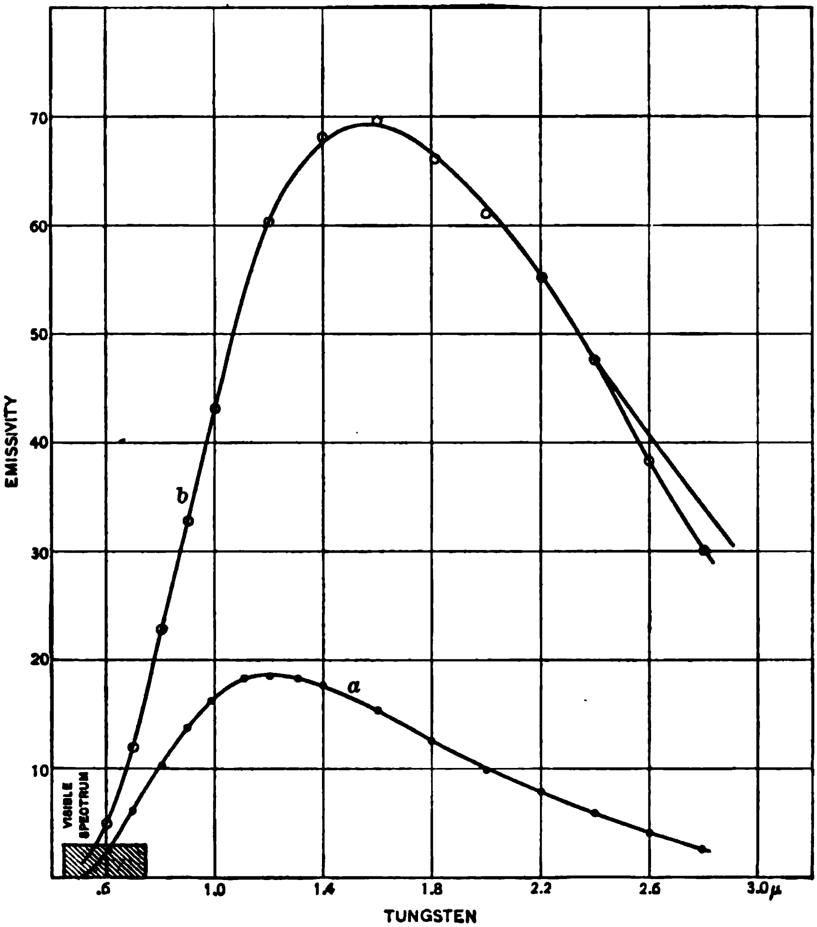

Fig. 2

In Fig. 2, curve *a*, is given the spectral energy curve of a new 110-volt, 32-candlepower tungsten lamp when on a normal operation of 55 watts. The mean value of the radiation constant for this lamp was previously computed[1] to be about $\alpha=6.5$, the variations in the individual computations being rather large. The spectrometer calibration has just been recomputed, which is more accurate than the one then employed. The new computation of this radiation constant is not sufficiently different from the old one to warrant a revision of the data then published, although the individual computations are in closer agreement. The new value of the $\lambda_{max}=1.225\mu$ (old $\lambda_{max}=1.257\mu$) and the new $\alpha=6.2$, the shift in the new calibration curve being about 0.02μ toward the short wave lengths. On the basis of the new calibration curve the wave lengths of maximum emission are too large by about 0.02μ. The radiation constants are also too large by 3 per cent to 5 per cent. Since the individual computations vary by this amount, and since different samples of the metal filaments seem to be subject to variation, the old values are probably as trustworthy as would be the revised ones. The experimental data does not indicate a variation of the constant "α" with wave length. For, at any temperature, the values of "α" are all high or all low irrespective of the wave lengths selected in the computations.

The reflection curve and the radiation constant ($\alpha=6.2$) are in close agreement with that of platinum. We are therefore in a position to make comparisons with platinum of which the radiation constants are fairly accurately known. Using the $\lambda_{max}T=2620$ of platinum, and the observed $\lambda_{max}=1.225\mu$ of tungsten, the operating temperature of the aforesaid lamp was 1870° C. Féry and Chéneveau (Compt. Rend., 149, 777, 1909) by using radiation methods obtained 1875°.

From the observed radiation curve *a*, Fig. 2, we can obtain the black body curve, *b*, at the same temperature, by dividing the observed emissivities by the observed absorptivities (100-reflectivity) of tungsten given in Fig. 1. The maximum emission lies at about $\lambda_{max}=1.45\mu$ from which the computed temperature is about 1760° C. This value is no doubt somewhat too low, because no account was taken of the loss by diffusion in the reflection curve at 0.6 to 2μ. Using the reflectivity values of platinum which are in all probability higher than the true values of tungsten, the $\lambda_{max} = 1.38\mu$ in place of $\lambda_{max} = 1.45\mu$ and $t = 1860°$ C, which is probably too high. The computed values of α, from curve *b*, Fig. 2, vary from 4.6 to 5.5 while the experimental value for a "black-body" is $\alpha = 5$. This shows that curve *b* is not a true "black-body" radiation curve. There are two evident reasons for this discrepancy. First, the observed curve *a* has not been corrected for absorption by the glass walls of the lamp, which would give an emissivity at 2.5μ somewhat as shown by dotted lines in Fig. 2. Second, the reflectivity is not known with sufficient accuracy at 1.5 to 2μ (because of diffuse reflection due to the fine pores in the specimen examined) where a small error in the reflectivity has a very large effect in the position of the maximum of the radiation curve. If it were not for this difficulty, this method could be used for estimating temperatures of metal filaments of known reflecting power (using perfect mirrors for determining the reflectivity), but of which it is impossible to measure the temperature directly. Since the emissivity and the reflectivity are functions of the refractive index and of the absorption coefficient, and since in considering the emissivity we are not concerned with the scattering effect, it does not seem necessary to consider the question of the "blackening" of the radiation due to the porosity of the filament, so long as the size of the pores are of the same magnitude as the wave length of the emitted light. This case seems to be different from the experiment in which the mechanical scratches, made in a strip of incandescent metal, show a higher emissivity than the outer surface. The present observations and those of Waidner and Burgess[5] seem to indicate that on "normal" operation the tungsten filament is at a temperature of 1850° C to 2200° C.

MOLYBDENUM

The area of the mirror examined was 5 mm x 17 mm. The reflecting surface had a very much higher polish than the sample of tungsten just described. To the eye it was apparent that the molybdenum had a higher absorption than the tungsten mirror. This is illustrated in the bolometric comparison, shown in Fig. 1, which indicates a reflectivity of only 46 per cent in the yellow, which rises abruptly to 85 per cent at 2.5μ beyond which point the reflectivity gradually increases to 95 per cent at 10μ. The specific resistance of two samples of molybdenum wire, drawn to a uniform diameter, was determined by Mr. Dellinger. The wires were respectively 15 cm and 20 cm in length, 0.627 mm and 0.815 mm in diameter, and the corresponding specific resistance was .000 006 4 and .000 006 2 at 21°.5. This is about 3.6 times the resistance of copper and practically the same as that of tungsten. From this it appears that the reflectivity of molybdenum should be as high as that of tungsten at 12μ. The observations indicate the opposite condition. No systematic errors could be detected in the observations and the only explanation which can be offered at present is that the size of the reflecting surfaces was too small to establish a true absorption to a greater accuracy than 2 per cent at 12μ. This, however is not a large discrepancy when it is recalled that in some of the earlier work, using larger mirrors of known curvature, errors almost as large as these are on record.

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[5] Waidner and Burgess, this Bulletin, **2**, p. 319.

The reflectivity curves of molybdenum and tungsten are so nearly alike that from a consideration of their emissivities and luminous efficiencies there seems to be no great choice in the use of these two metals in incandescent lamps. On the other hand, from a consideration of their physical properties, the molybdenum filament would be the preferable because it seems to retain its toughness and its ductility, in contrast with tungsten which seems to become crystalline and brittle after being operated, for a while, at a high temperature. The melting point of molybdenum is quite high, and it is principally a question of overcoming certain physical weaknesses, such as disintegration, in order to make this material useful for incandescent lamp filaments.

GRAPHITE

Two samples of graphite were examined, the one being the natural mineral from Siberia. Its reflecting surface was 4 cm x 5 cm. The second sample, curve *b*, Fig 3, was a longitudinal section of a rod, 8 mm in diameter, of Acheson's graphite. It could not be burnished free from pores which were rather large, and which caused a scattering of the radiation, out to 4μ in the infra-red. Beyond this point it reflects as highly as the natural Siberian mineral, shown in curve *a*, Fig. 3. The natural mineral was very compact, but showed the rays and fibrous structure of the original plant or tree from which it was formed. It was burnished or "polished" on a semi-matte piece of plate glass. A thoroughly ground glass was too rough, while the smooth plate was found equally inapplicable. The partly ground glass seemed to hold just sufficient material to work into the softer parts without accumulating sufficient loose material which would roughen the surface. The glass plate was kept wet with clean water and by the application of some pressure it was possible to prepare a very highly polished surface.

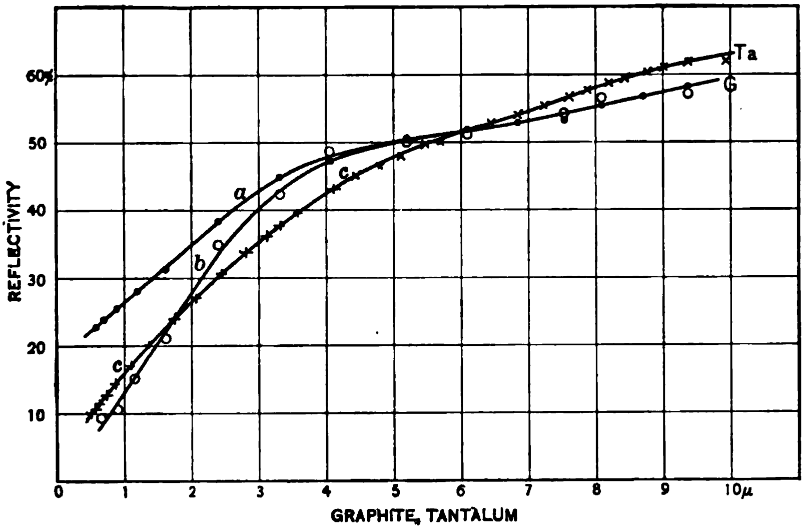

Fig. 3

The reflectivity is 23 per cent in the yellow, gradually increasing to 63 per cent at 10μ. From the low reflectivity at 2μ in the infra-red there results a high emissivity (in contrast with the metals), hence the graphatized carbon filament can not have the same luminous efficiency as the tungsten lamp at the same temperature, although it has the higher emissivity in the visible spectrum.

TANTALUM

The utilized area of the tantalum mirror was 9 mm x 14 mm. In spite of its excellent polish, it showed an exceedingly low reflectivity throughout the spectrum, as compared with pure metals.

The curve *c*, in Fig. 3 represents three series of observations, using different adjustments, the measurements usually agreeing to one part in 100 to 200. In the visible spectrum the reflectivity is only 10 per cent, which gradually increases to 63 per cent at 10μ. There is no indication of an approach to constant reflectivity, in in the infra-red, such as obtains in pure metals. Subsequent correspondence with the maker showed that this surmise of an impure metal was correct. The surface was rendered impure by working and polishing which, by the action of gases, formed an exceedingly hard surface layer. From the writer's experience it appears that the ease with which a tantalum mirror becomes contaminated in polishing depends upon the previous history of the metal. For example, the regulus of tantalum obtained from Von Wartenberg[6] had never been rolled or hammered, and it was found that, in polishing it, any contamination, such as for example, the blackening caused by a film of oil, was easily removed. On the other hand, a film of oil on the mirror just described, which had evidently been worked down from a regulus (Fig. 3, *c*) formed a brown coating which was removed with great difficulty.[7] The rear side of this mirror was therefore ground flat on fine emery paper, which for the final polish was covered with a layer of alcohol and graphite. By stroking lightly and lifting the mirror soon after the alcohol had entirely evaporated, a clean surface was produced which was almost free from scratches. The old surface, of which the reflectivity is given in Fig. 3, was so hard that it could not be polished by this method.

The contrast between the reflectivity of the old contaminated surface and the new surface, polished as just described, is shown in Fig. 4. Curve *c* gives the reflectivity of the new surface as produced by the fine dry emery paper, the scratches being quite deep. Curve *a* gives the reflectivity of the same mirror after giving it the final polish with graphite and alcohol, when only very fine scratches remained. In the latter case the scattering is almost eliminated, and the reflectivity rises abruptly from 39 per cent in the yellow to 85 per cent at 2.5μ, beyond which point the rise is gradual to 94 per cent at 9μ. The theoretical reflecting power, at 12μ, computed from the electrical conductivity, is about 95.7 per cent.

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[6] Von Wartenberg, Verh. Phys. Gesell., **12**, p. 121; 1910. He found that tantalum was not contaminated by polishing.

[7] See further a recent investigation by Parani, Verh. Phys. Gesell., **12**, p. 301, 1910, who likewise finds that tantalum is easily contaminated by gases.

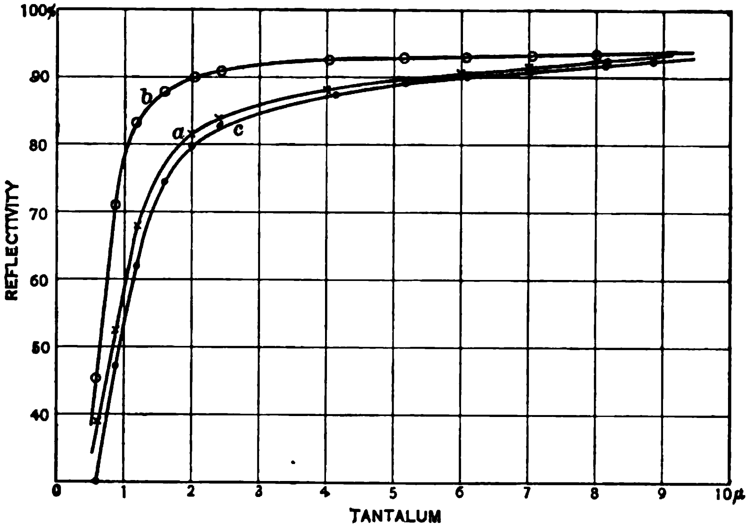

Fig. 4

Through the kindness of Dr. Von Wartenberg an opportunity was granted to examine the tantalum regulus mirror used by him in determining the optical constants in the visible spectrum. The area of surface which could be used was only about 2.5 mm x 3 mm, and hence it was impossible to obtain the absolute reflectivities with high accuracy. There was no difficulty in obtaining the relative values for different parts of the spectrum, which is the point of most interest. The surface of the mirror was perfectly free from scratches. The reflectivity, which is shown in curve *b*, Fig. 4, rises even more abruptly to high values than was found in the first sample. In this respect, pure tantalum, zinc, and silver stand unique among the metals. Because of the steepness of the reflectivity curve, the emissivity of tantalum in the visible spectrum must be more selective than obtains in tungsten and molybdenum. Furthermore, since the reflectivity of pure tantalum is higher than that of tungsten at 1 to 2μ, it must have the higher luminous efficiency.

The reflectivity of the regulus of pure tantalum as observed by two methods (Wartenberg computed R from the "optical constants") is about 45 per cent in the yellow. The other mirror appeared much darker, so that the lower reflectivities as shown in Fig. 4 are to be attributed to impurities. The tantalum regulus appeared as bright as the prism of tungsten already described. The most casual observation shows that the tungsten filament has a much whiter metallic luster than a tantalum filament. This may be due to contamination in drawing the tantalum wire, especially if drawn with oil as a lubricant. It appears that in tungsten all the impurities can be driven off at high temperatures. This is not necessarily true of tantalum, which occupies an anomalous position in the scale of luminous efficiencies of metals.

From the observations of Waidner and Burgess, who found that the "normal" operating temperature of tantalum is about 2000 C, it is evident that its low luminous efficiency is not due to a low operating temperature, such as would be necessary with platinum.

Incandescent lamps of tungsten and osmium have an efficiency of about 1.25 watts per candle, while for no apparent reason tantalum must be classified with graphitized carbon with an efficiency of about 2 to 2.5 watts per candle.

The foregoing data on the reflectivity of tantalum and graphite (Fig. 3) shows that this classification is consistent. The radiation constants of these two substances are almost the same (total radiation; tantalum proportional to the 5.3-power of temp.; graphitized filament proportional to the 5.1-power of temp.), and the manner in which they differ is in the right direction, since graphite is a nonmetal. Hence, while it was somewhat contrary to expectation to find such a low reflectivity in the infra-red for impure tantalum, this is not inconsistent with other data such as the radiation constants.

There seems to be a prevailing notion that the polish of the metal filament is of great importance, but it is not apparent how roughness or scratches can cause a "blackening" of the radiation by successive reflection within the cavities so long as the latter are of the order of the wave length emitted. It is the absorption coefficient and the refractive index that must be considered. This is especially conspicuous in tantalum filaments. When new they have a brownish luster, while the filaments of old lamps are decidedly black. Similar filaments of osmium retain their gray appearance even after becoming crystalline. Under the microscope the crystalline tantalum filament appears much darker than tungsten, although the actual polish of the crystal surfaces of the latter is much higher. Some crystals appear as dark as highly polished jet or fine grains of stibnite, which has a reflectivity of only about 35 per cent. This low reflectivity in the visible spectrum produces a high emissivity, but, contrary to the properties of the pure material, the reflectivity continues low (emissivity high) in the infra-red, which tends to lower the luminous efficiency.

The ideal solid illuminant must fulfill the conditions of a high operating temperature, and a high emissivity in the visible spectrum. As shown in Fig. 1, of all the metals thus far examined, tungsten approaches nearest to the fulfillment of these conditions.

ANTIMONY

It was found impossible to produce a perfect mirror of antimony, so that the absolute values obtained have little weight. Since the main object in the present work is to show the relative values of reflectivities in the visible as compared with the infra-red, the results obtained on several antimony mirrors are here recorded. As with all the other metals, larger surfaces, either plane or of known curvature, must be used for high accuracy in the absolute values.

Two samples of antimony were examined, the one being a mirror (5 mm x 17 mm) polished upon a cleavage plane of a large crystal of the metal (from Kahlbaum), the other being a mirror formed in vacuo by cathode disintegration. The reflectivity of the polished cleavage piece is shown in curve *a* of Fig. 5. The reflectivity is low, due to the presence of numerous large-sized pores which resulted in the polishing. Two cathode mirrors were also examined. The first one contained small holes caused by dust particles on the glass surface, which seemed to permit radiation from the rear surface of the glass (2 mm in thickness) to return on its path, thus causing a wavy reflection curve with maxima of about 65 per cent at 1.2μ, 2.5μ, and 4μ, and minima of 55 to 60 per cent at 2μ, 3.3μ, and 6μ, beyond which point the reflectivity increased gradually to 68 per cent at 9μ. On removing the rear mirror surface the maxima and minima were destroyed. A second mirror (5 mm x 17 mm), free from dust holes, and with the rear surface of glass free from metal, was examined, the data being plotted in curve *b*, Fig. 5. The reflectivity rises from 53 per cent in the yellow to a fairly uniform value of 72 per cent at 9μ.

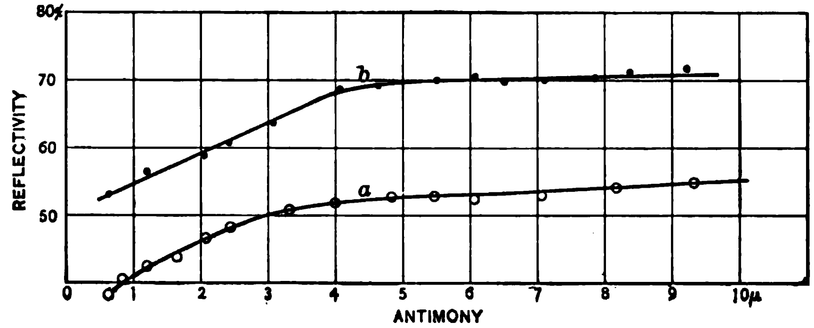

Fig. 5

In view of the difficulty in producing a mirror which is free from carbon, by the cathode discharge, and in view of the fact that the mirror seemed darker than one would expect, judging from the appearance of the crystals, it seems probable that the reflectivity is somewhat higher than here recorded. However, in view of the fact that antimony departs considerably from the true metals, the low reflectivity throughout the spectrum is probably to be expected, as will be noticed presently in several other metals which lie on the border line between the electrical conductors and the insulators.

In conclusion, it may be added that cathode mirrors of antimony are easily produced in 5 to 7 minutes, by using a heavy current. The tendency is for one to continue the discharge for a longer period than this, with the resultant oxidization of the central part of the mirror. By using a residual atmosphere of hydrogen and a low current, excellent large-sized mirrors are produced in half an hour.

RHODIUM

The sample examined was kindly loaned by Dr. Von Wartenberg. The area of the surface examined was 5 mm x 5 mm. Several small blowholes were present, which, with the smallness of the surface, did not permit high accuracy in the absolute values of the reflectivities. The reflecting power (Fig. 6), *Rh*, rises abruptly from 77 per cent in the yellow to 92 per cent at 2.5μ, beyond which point the rise is gradual to about 94 per cent at 9μ.

IRIDIUM

The mirror examined was a thick plate of the metal, which in the polishing had not been perfectly freed from pores, which caused scattering. The reflectivity in the yellow was only 53 per cent, which increased to 75 per cent at 2μ and to 90 per cent at 8μ. This same plate was examined several years ago[8] when it had a finer polish. The reflectivity, Fig. 6, *Ir*, was found to increase from 79 per cent at 1μ to 95 per cent at 9μ. Its reflectivity seems to be somewhat higher than platinum in the visible spectrum.

IRON

The sample of iron examined had a purity of 99.8 per cent. The chief impurities were .15 per cent copper, .02 per cent manganese, and .02 per cent carbon. The sample took a high polish and reminded one somewhat of palladium in its general appearances. The reflectivity, Fig. 6, *Fe*, rises gradually with increase in wave length and, throughout the spectrum, the values are about 2 per cent higher than the values previously observed on steel by Hagen and Rubens.

MAGNESIUM

The mirror examined had a surface of about 1.2 cm x 2.5 cm. It was polished with considerable difficulty. A highly polished surface free from scratches was finally obtained by wet-grinding on fine emery paper, using tin oxide ("putty powder") and then (dry) polishing the surface on chamois skin with a little putty powder. This procedure prevented the formation of a film of oxide. However, the surface was not entirely free from blisters, so that the reflectivities are somewhat higher than recorded in Fig. 6, *Mg*. The reflectivity curve is somewhat different from that of a pure metal, especially of aluminum. (See this Bulletin, vol. 2, p. 470.) The alloy of aluminum and magnesium, magnalium, has a reflectivity curve which falls between these two metals.

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[8] See this Bulletin, **2**, p. 470, 1907, where the reflectivity data of this and numerous other metals is tabulated.

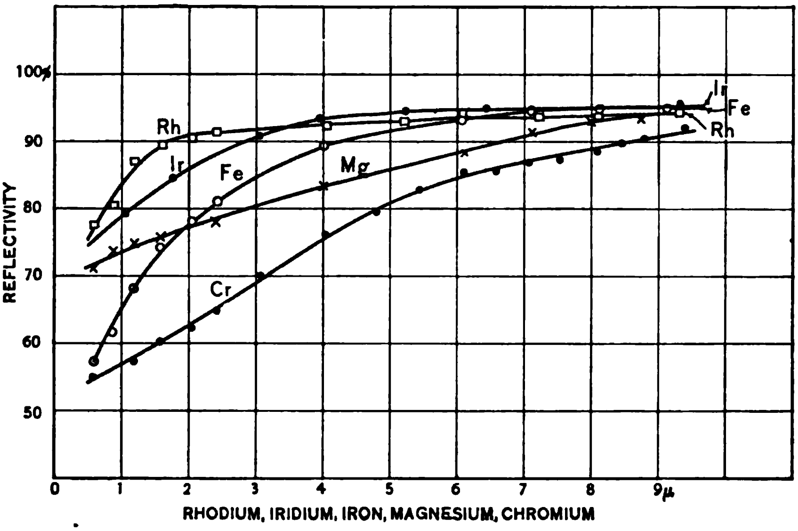

Fig. 6

CHROMIUM

The sample of chromium was sawed from a lump of the metal made by the Goldschmidt process. The material was quite crystalline, but took a fairly high polish, excepting the usual pores which were rather large as compared with those of the sample of tungsten, just described. The reflection curve, Fig. 6, *Cr*, increases gradually from 55 per cent in the yellow to 91 per cent at 9μ. Judging from previous experience with other metals, it seems quite certain that, for a perfect mirror surface of noncrystalline material, the reflectivity of chromium would be higher in the yellow, as observed by Wartenberg. While part of the low reflectivity of chromium is no doubt due to diffuse reflection, out to 5μ, it is to be noted that this metal produces acid compounds, just as was observed with antimony, and in its general properties can not be classed with the true metals. Hence its unusual reflection spectrum is to be expected.

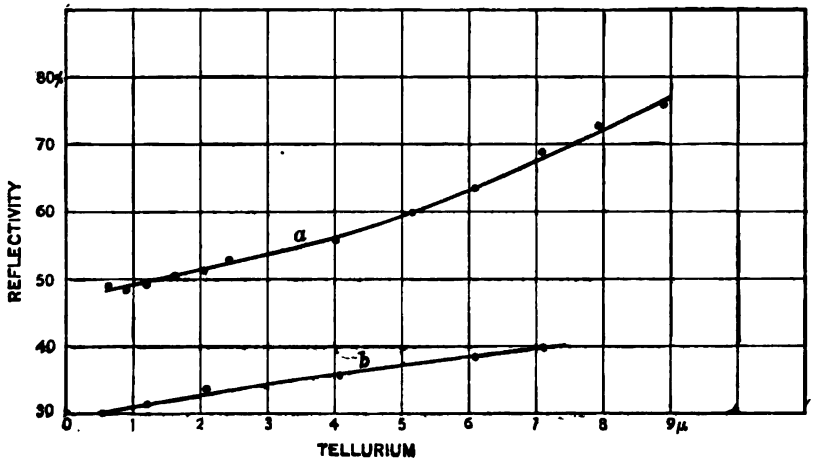

Fig. 7

VANADIUM

The sample examined was kindly loaned by Dr. Von Wartenberg. The surface was plane, highly polished, and the area examined was about 5 mm x 5 mm.

The reflecting power, curve *c*, Fig. 8, rises gradually from 58 per cent in the yellow to 92 per cent at 9μ. In this respect it is very similar to chromium and iron, Fig. 6. This is to be expected since they fall in the same group in the Mendelejeff series.

TELLURIUM

A knowledge of the reflectivity of tellurium is of interest because it occurs on the border line between metals and nonmetals and has a high electrical resistance. It is usually found in a highly crystalline state, and it is therefore difficult to polish a surface free from pores. The reflectivity curve of such a mirror is given in curve *b*, Fig. 7. It is of interest only in showing the general trend of the reflectivities in various parts of the spectrum. The absolute values would be very much higher if a correction could have been made for the loss by scattering caused by the roughness of the surface..

The best mirror used in the present examination was produced by the cathode discharge in hydrogen. It was found that unusually large-sized mirrors can be deposited in this manner, the time required being about half an hour. Thin deposits of tellurium transmit a reddish-brown light, which would indicate a low reflection beyond the red or a minimum reflection in the red. This is illustrated in curve *a*, Fig. 7, where at .8μ the reflectivity, after repeated observations, was found to be slightly less than in the yellow. While this might be due to the lack of knowledge of the true value of the reflectivity in the visible spectrum of the silver comparison mirror, the color of the transmitted light seems to indicate such a minimum. The occurrence of a reflectivity minimum so far in the red is unusual in the true metals. However, the characteristics of tellurium are so different from the usual ones of true metals, that such an unusual reflecting power is probably to be expected.

The construction of a thermopile having large surfaces usually results in a sluggish instrument because of its great heat capacity. It has been suggested to deposit by cathode discharge two metals (for example, Te-Cu) upon some material which can afterwards be removed. These two films of metal are to overlap along one edge, which forms the active junction. The thermoelectric power of tellurium is very high; and in view of the ease with which a film of this metal can be deposited, it might prove satisfactory as a surface thermopile.

SILICON

A knowledge of the reflectivity of this element is of interest because it belongs to the nonmetals or insulators. Two samples were examined. The polishing was done on a fine grade of emery paper covered with a mixture of tin oxide and a little graphite. The one sample, from Kahlbaum, curve *b*, Fig. 8, was quite homogeneous and took a very high polish, free from scratches. The second sample from the Carborundum Company, curve *a*, Fig. 8, was less homogeneous, its hardness was greater and it took a poor polish. The crystals as they come from the furnace are of a bluish color, as was also true of the highly polished remelted sample here examined. This causes a high reflectivity in the visible ($R = 34$ p. c. at .5μ; 30 p. c. at .75μ; 28 p. c. at 1μ) spectrum, which decreases rapidly to a uniform value of 28 per cent beyond 1μ in the infra-red. The lower value of 24 per cent in curve *a* is due to the porosity and to the consequent diffuse reflection by this sample of silicon. From an examination of these two samples it appears highly improbable that the absolute values of the reflectivities, to 10μ in the infra-red, are much greater than 30 per cent. It was noticed in Fig. 3 that the reflectivity of graphite continues to rise gradually with increase in wave length. The carbide of these two elements, carborundum SiC, as well as the oxide SiO_2, have the most remarkable[9] reflection spectra yet observed, with bands of selective reflection which are as high in value as the reflectivity of pure metals.

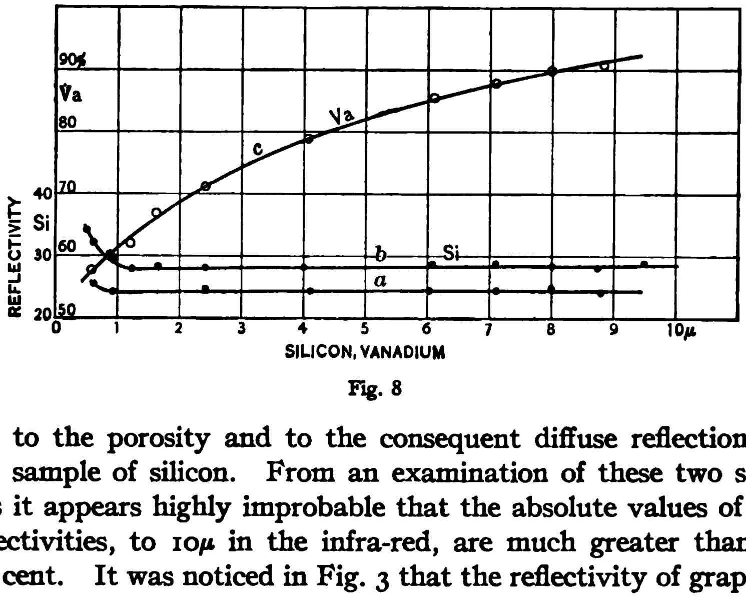

Fig. 8

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[9] This Bulletin, 2, p. 476; 1907.

SUMMARY

The reflecting power of various metals has been examined, including tungsten, tantalum, and molybdenum. By comparing these metals with silver, of which the reflectivity is known, the absolute reflectivities have been determined.

Each individual substance required a special mode of polishing in order to produce a smooth surface free from contamination. These methods are indicated in the text.

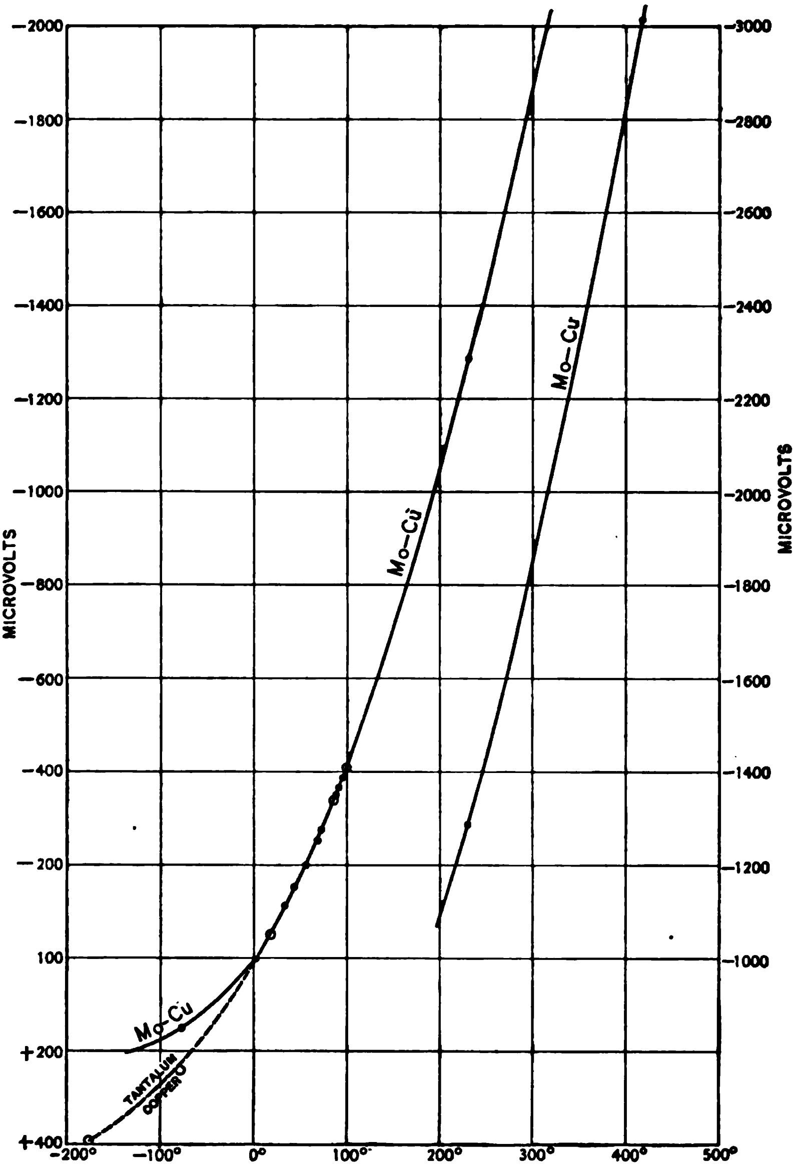
It is shown that, in common with all the other pure metals previously examined, the present series has a low reflectivity in the visible spectrum which increases rapidly to high values in the infra-red. The reflectivity curves of tungsten and of molybdenum are so nearly alike that from a consideration of their optical properties there is no great choice in the use of these two metals in incandescent lamps. Since molybdenum is tough and tungsten is brittle (i. e., becomes brittle after being operated at high temperatures), it remains to be seen whether other physical difficulties can be overcome in the former metal to enable its introduction as an illuminant.

The reflectivity curves show that the high efficiencies of the metal filament lamps is due to their low reflectivity (true absorption, and not diffuse reflection, is meant) in the visible spectrum and to a high reflectivity in the infra-red.

A high operating temperature is also necessary for a high luminous efficiency in metal filament lamps. This is exemplified in the difference in the efficiencies of platinum and tungsten lamps.

In tungsten the low reflectivity in the visible spectrum results in an emissivity of almost 50 per cent, while in the infra-red the emissivity is less than 10 per cent of an ideal radiator.

The ideal solid illuminant giving a high luminous efficiency must fulfill the condition of a high operating temperature, a high reflectivity (hence low emissivity) in the infra-red and a low reflectivity (high emissivity) in the visible spectrum. The pure metals, tungsten and molybdenum fulfill these conditions more exactly than any other known metals, excepting tantalum, which as a lamp filament, however, does not have the optical properties of the samples described in this paper.



THERMAL EMF. MOLYBDENUM COPPER

Fig. 9

Thus far it has been impossible to obtain a large-sized sample of pure osmium, to determine its reflectivity.

In conclusion, the writer expresses his appreciation of the courtesy of Dr. Von Wartenberg in submitting his samples of tantalum, rhodium, and vanadium for examination.

NOTE I

ON THE THERMOELECTRIC PROPERTIES OF MOLYBDENUM

Having the requisite apparatus and pure wire at hand, it seemed of interest to determine and place on record the thermoelectric behavior of molybdenum. This seemed especially true since its physical properties do not warrant a separate and extensive investigation; and yet this data is of importance for comparison with other metals.

The methods and instruments here employed were described in a previous paper on the thermoelectric properties of tantalum and tungsten.[10] The wire used (specific resistance given on a previous page) was .627 mm in diameter and about 25 m long. Copper wires .2 mm in diameter were wound tightly around the ends of the molybdenum wire and soldered with tin. For the melting points of zinc and tin the junction was in a thin glass tube. Above 600° the molybdenum oxidized so rapidly that no measurements were made on its emf. For temperatures as high as 419° (m. p. zinc) the metal shows no oxidation. The observations were extended to $-78^\circ.5$ C, which temperature was obtained with a thick solution of carbon dioxide snow and ether. The results are given in Fig. 9, which includes tantalum. Between 0° and 100° these two metals have almost the same thermoelectric power. It is to be noticed, however, that they are *opposite in polarity*. In a copper-tantalum couple the direction of the current is the *same* as in copper-constantan, while in copper-molybdenum the direction of the current is *opposite* to that of a copper-constantan couple. Between 0° and 100° the thermoelectric power of the molybdenum-copper couple is 4.4, between 100° and 200° it is 6.6, and between 200° and 400° it is 9.3 microvolts per degree. The thermoelectric power, between 0° and 100°, is about one-tenth the thermoelectric power of copper-constantan.

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[10] This Bulletin, 6, p. 107; 1909.

NOTE II

PRESERVATION OF SILVER MIRRORS

Silver-on-glass mirrors and especially mirrors made by grinding and polishing the metal itself become tarnished and turn brown very rapidly when exposed to the air in the laboratory. The question naturally presents itself whether or not the slight difference in reflectivity of molybdenum and tungsten, described on a previous page, is caused by a systematic error due to a gradual deterioration of the silver comparison mirror. The electrical conductivity indicates that the reflectivity of molybdenum should be slightly higher than tungsten. Since the two metals were examined in rapid succession on the same day, the question of deterioration of the silver mirror is negligible. This silver-on-glass mirror was prepared just before the observations were made, but no difference could be detected between it and mirrors now almost two years old. The latter mirrors, some of them 15 cm in diameter, also a mirror of solid silver, were prepared in the earlier part of 1908 and were at once placed in a large desiccator containing vessels of phosphorous pentoxide and potassium hydroxide. When not in use the mirrors are kept in this manner. A large mirror spectrometer has its optical parts similarly inclosed and the mirrors appear as white as when made two years ago. This simple device of keeping the mirrors in dry air seems to preserve them indefinitely, in marked contrast with mirrors standing in the open, when the surface tarnishes in a very short time.

NOTE III

COMMENTS ON RADIATION LAWS OF METALS

In a previous paper [11] the spectral radiation constant, "α," of various metals was described. This "constant" was found to vary with the temperature and theoretical reasons were given to account for this variation. The data presented in the present paper support the experimental data then obtained, but lead to a different and a more plausible explanation of the cause of the variation in "α" with temperature. If in the previous experiments the equation representing total radiation had been considered, $S=\sigma T^{\alpha-1}$, then we would have had to consider the constant "σ" as well as the constant "α." The constant "c_2," in the equation $c_2=\alpha\lambda_{max}T$, also involves the temperature, as well as other factors, so that "α" was the only constant that could be investigated, as described in the aforesaid paper.

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[11] Coblentz, this Bulletin, 5, p. 339; 1909. See p. 367 for a discussion of the radiation from platinum.

Assuming[11] a value of $\alpha=6$, the radiation from platinum observed by Lummer and Kurlbaum[12], shows a variation in the constant of total radiation from $\sigma=8.24$ to $\sigma=11.16$ for an increase in temperature of about 1275 degrees.

It seems apparent that "σ" can not be considered constant, for it indicates the emissivity per unit area of a surface radiating under specific conditions. Now if those conditions vary, as is true of the metals in which the absorptivity (at any wave length) is a function of the temperature, it would seem that the "σ" can not remain constant, but must increase with rise in temperature. The coefficient of emissivity, "σ," must therefore be rigidly defined, just as is true of the resistivity.

The constant, α, in the Wien equation $E=c_1\lambda^{-\alpha}e^{-c_2/\lambda T}$ and as tentatively assumed in the aforesaid computations, relates to a specific region of the spectrum; and irrespective of the writer's published data, experiments by others show that the emissivity of metals at any wave length in the infra-red is affected by the temperature, i. e., it has a temperature coefficient. But this is not all. At low temperatures the maximum emission, E_{max}, falls in the region of 3 to 6 μ where the reflecting power at a given temperature is practically constant and we have to consider only the change in the radiation constant, "α," due to the temperature coefficient of the reflectivity. At high temperatures the E_{max} falls in the region of 1.5 μ (see Fig. 1), where at any given temperature the reflectivity changes rapidly with wave length; and as it shifts toward the short wave lengths the E_{max} must increase by a different law (from the Wien equation $E_{max}=B\,T^{\alpha}$) from what it did when at 3 to 6 μ. In the region of 1.5 μ the temperature coefficient is small, but the absorption (100-reflectivity) varies rapidly with wave length, while beyond 3 μ the conditions are exactly the reverse. In both cases the emissivity, E_{max}, increases in a different manner than postulated by the simple radiation formulas.

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[12] Lummer and Kurlbaum, Verh. Phys. Ges., Berlin, **17**, p. 106; 1898. They assumed a value of $\alpha=5$ and found a variation of $\sigma=4.28$ to $\sigma=19.64$ for a temperature change of about 1275°.

Now, from the Wien equation, $E^{\lambda} = c_1\lambda^{-a}e^{-c_2/\lambda T}$, the radiation constant "α" is computed from the equation (Eq. 1)

$$a = \frac{\log E - \log E_{max}}{\log e - \frac{\lambda_{max}}{\lambda} \log e + \log \frac{\lambda_{max}}{\lambda}} \qquad \text{(Eq. 1)}$$

where E and E_{max} are the emissivities at the wave lengths λ and λ_{max}, respectively. It will be noticed that the temperature of the filament does not enter into this equation. From the most recent work of Hagen and Rubens, (Phys. Zeit. 2, p. 139, 1910) it appears that in the region extending from the visible to 3 μ the temperature coefficient of emissivity is extremely small, and the observed variations in "α" with temperature, as computed from the above equation, must be due to some other cause than a true temperature coefficient of emissivity. This cause is not difficult to find if we turn to the reflectivity curves, Fig. 1. At low temperatures, when λ_{max} falls in the region of 2 μ, the E_{max} is but slightly affected by the temperature coefficient of emissivity, and since the reflecting power varies but slowly with the wave length, the E_{max} will be closely that required by the Wien equation ($E_{max} = B\ T^{a}$). At high temperatures when the λ_{max} falls in the region of 1.2 μ, the E_{max} falls in the region where the reflectivity changes rapidly with wave length, and consequently the value of E_{max} must increase at a higher rate than required by the equation $E_{max} = B\ T^{a}$. The difference between $\log E - \log E_{max}$ (Eq. 1) must therefore be less than would otherwise be the case, due to this fact, and the decrease in "α" with temperature when computed from the above equation must necessarily follow, as observed.

From the reflectivity curves this seems a plausible explanation. Hence, an accurate value of "α" cannot be computed from the Wien equation as expressed in (Eq. 1). However, from the close agreement between the values of "α" of platinum by this and by more direct methods, it is evident that the errors resulting from the use of Equation 1 are not serious. The aforesaid work has shown in a fairly quantitative way that the constant "α" of tungsten is much higher than that of platinum and of carbon. The great suppression of the radiation of tungsten as compared with carbon in the infra-red is another proof of this. The Wien spectral energy curves, using different values of "α," illustrate this same behavior, as may be easily verified by plotting the data given in Table I, this Bulletin, 5, p. 347.

It seems evident that any spectral radiation formula which can be set up must contain factors which will take into consideration not only the variation in emissivity with temperature, but also the variation in the absorptivity, which is a function of the wave length and the temperature. Whether the constant "α" really varies [13] as found in my previous paper where the Wien equation was tentatively assumed, or whether the constant "σ" varies, or whether both vary, is not the all important question at this stage of our knowledge. The most important thing for the present is to get further experimental data [13] on total and spectral radiation, using wide strips of such metals as platinum and tungsten, and suitable means to measure the temperatures. In this manner it is hoped to contribute more accurate data in the near future.

Summary.—For metals the physical facts are:

(1) An extraordinary variation in their reflectivity, from the visible to about 2μ, beyond which point the reflectivity increases but slowly with wave length.

(2) A small temperature coefficient of emissivity from the visible to 3μ, beyond which point the temperature coefficient increases rapidly with wave length.

(3) For the black body the position of maximum emission in the spectral energy curve shifts, with the rise in temperature, toward the short wave lengths by a given amount, because only the temperature enters the problem and $\lambda_{max}T = \text{const.}$ Furthermore the height of the maximum emission increases by a fixed amount $E_{max} = BT^{\alpha}$. The total radiation progresses as $S = \sigma T^{\alpha-1}$. The constants "α" and "c_2" are concerned in the slope of the

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[13] This conclusion was evident in my previous paper. This Bulletin, 5, p. 379; 1909.

spectral energy curve, while "σ" defines the total emissivity per unit area of the radiator. In the pure metals, the variation in E_{max} and λ_{max} will be affected (by opposite amounts) by (1) and (2), and as already mentioned in the text, these formulæ, just mentioned, must be modified to take account of these facts.

(4) The cause of the constancy of "α," as found in the visible spectrum and of its variability as found in the infra-red, is probably due to the fact that in the very limited region of the visible spectrum λ_1, and λ_2 are close together, and, in the computations, they are *taken the same at different temperatures.* Moreover no temperature coefficient of emissivity has yet been definitely established in this region. On the other hand, in the infra-red, λ_1 and λ_{max} are far apart, and λ_{max} *is different for different temperatures.* Furthermore, the λ_{max} is affected by a temperature coefficient of emission, and by a rapid change in emissivity due to a rapid variation in the reflecting power, especially in the region of 1 to 1.5μ.

WASHINGTON, May 28, 1910.

THE ACTION OF SUNLIGHT AND AIR UPON SOME LUBRICATING OILS

By C. E. Waters

In 1885 Schaal[1] patented a process for the manufacture of soaps by the action of air upon mineral oils in the presence of alkaline substances. This was based on an older observation of Engler's.

In 1891 Zaloziecki[2] studied the oxidation of petroleum by means of air. By blowing cold air through the oil the oxidation was slight, but was greatly increased in the presence of sodium hydroxide. The acidity shown by methyl orange, as opposed to phenolphthalein, he believed to be due to the oxidation of mercaptans and organic sulphides, and not to the presence of traces of the acid used in refining.

Schestopal[3] found that illuminating oils absorbed several volumes of oxygen at room temperature when inclosed in sealed tubes laid horizontally. He pointed out the bearing this had upon the treatment of kerosene in agitators.

Holde[4] exposed mineral and vegetable oils to the air for a long time, studying changes in the viscosity, specific gravity, etc. He found that the changes were much less for mineral than for vegetable oils.

Haack[5] believed that the oxidation observed in refining oils was due to the combined action of sulphuric acid and air. This idea was upheld by Kern.[6] Other papers bearing upon the question of oxidation by atmospheric oxygen were published.[7]

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[1] D. R. P. 32705; Chem.-Ztg., **9**, p. 1520; 1885.

[2] Z. angew. Chem., **1891**, pp. 416–19.

[3] Chem.-Ztg., **15**, pp. 352–4; 1891.

[4] Mitth. kgl. techn. Versuchsanst., **10**, pp. 85–90; 1892; J. Soc. Chem. Ind., **11**, p. 619; 1892.

[5] Chem.-Ztg., **16**, p. 694; 1892.

Zaloziecki [8] studied the influence of light and air upon the acid treatment of kerosene. In some of his experiments he used colored glass. The general conclusion reached by him was that light and air should be excluded. Ostrejko [9] confirmed this work as to the effect on the color of refined petroleum, and also determined the increase in acidity due to oxidation. Wischin [10] thought that the darkening in color of kerosene was perhaps due to a molecular rearrangement of dissolved asphalt under the influence of actinic rays.

Hirsch [11] passed air through mineral oils in the presence of soda lye, and even after 12 hours at 70° could detect no change in the alkali, concluding from this that there was no oxidation. Aisinmann [12] found that the absorption of oxygen was very slight. It was also stated by Künkler and Schwedholm [13] that there was no increase in weight when mixtures of mineral oil with bone oil, olive oil, etc., were rubbed up with sand or pumice and exposed to the air. The resinification noticed was believed to be due solely to polymerization.

There can be no doubt, however, that oxidation really takes place. Charitschkow,[14] who states that the resinous products formed in petroleum on long standing under the combined influence of light, air, and moisture are nearly identical with those of Schaal, obtained sirup-like acids [15] by the action of air in the presence of alkalies. These acids, which are nearly insoluble in benzine and petroleum ether, he calls "polynaphthene," or "asphaltogenic" acids, the latter name being self-explanatory.

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[6] Chem.-Ztg., **17**, p. 706; 1893.

[7] Zaloziecki: Chem.-Ztg., **16**, p. 591; 1892. Holde: *Ibid.*, **18**, 704, pp. 1737, 1935; 1894. Hirsch: *Ibid.*, **18**, p. 1824.

[8] *Ibid.*, **19**, 875–7, 956–8; p. 1895.

[9] See J. Soc. Chem. Ind., **15**, p. 345; 1896.

[10] Chem. Rev. Fett-Harz-Ind., 1895, Nos. 26 and 27; J. Soc. Chem. Ind., **14**, p. 1039; 1895.

[11] Chem.-Ztg., **19**, p. 41; 1895.

[12] Dingl. pol. J., **294**, p. 658; 1894; J. Soc. Chem. Ind., **14**, p. 282; 1895.

[13] Seifensiederztg., **35**, p. 341; Chem. Zentr., 1908, II; 1859.

[14] Z. angew. Chem., **21**, p. 1155; 1908.

[15] Chem.-Ztg., **33**, p. 1165; 1909.

Meyerheim,[16] in this connection, thinks the increase in asphalt content with lapse of time is due to polymerization or to a change from the original colloidal condition to the insoluble form. His experiments were carried out in closed bottles two-thirds filled with oil. The changes in asphalt content in two oils, kept in the dark, in diffused light, and under the influence of radium emanations, were determined. After 8 months no difference due to the action of radium could be detected. In diffused light one oil showed a higher asphalt content than a control kept in the dark; the other oil showed the same content of asphalt as the control.

Molinari and Fenaroli [17] obtained unstable ozonides from petroleum hydrocarbons. They were precipitated from their solutions in benzine, ether, or chloroform by means of petroleum ether. They decomposed at 20° and changed at 35°–50° into a soft, red substance which was converted into a resinous mass at 105°.

An interesting observation bearing on the work described in this paper was made by Ackermann.[18] A sample of naphtha from Russian Turkestan was entirely thickened on exposure to the sun's heat for a whole year in an open vessel. Fresh samples of naphtha yielded 76.68 per cent of distillate between 20° and 310°, while the thickened oil yielded only 15.67 per cent of distillate.

In a paper entitled "Studies on the Carbenes" Mackenzie [19] shows that the action of light upon solutions of asphalt in carbon tetrachloride greatly increases the percentage of "carbenes" or insoluble bitumens. This is shown to be due to the formation of hydrochloric acid, which precipitates the carbenes.

The present writer was at the time determining asphaltic material in certain lubricating oils, and the above-mentioned paper, though on a somewhat remotely related subject, suggested the experiments herein described.

Three samples of oil were used. B and C were straight mineral oils; B was moderately dark in color, while C was much lighter colored and less viscous. D resembled B in color and viscosity, but contained approximately 0.5 per cent of fatty oil.

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[16] *Ibid.*, **34**, p. 454; 1910.

[17] Ber. d. chem. Ges., **41**, p. 3704; 1908.

[18] Chem.-Ztg., **34**, p. 440; 1910.

[19] J. Ind. Eng. Chem., **2**, pp. 124–127; 1910.

Duplicate samples of 20 g each were weighed into 150 cc Erlenmeyer flasks, loosely covered with caps to exclude dust and rain, and were exposed outside a window facing south for 23 days. Within 2 or 3 days the samples began to have a slight cloudiness, and after a week or 10 days the insoluble matter formed a cake on the bottom. After 23 days the contents of each flask were diluted with 50 cc of ligroin and after 36 hours the insoluble matter was filtered off in Gooch crucibles, washed with ligroin, dried at 100° and weighed. The following percentages of insoluble matter were found:

Sample	B	B	C	C	D	D
Insoluble (per cent)...........	0.77	1.03	2.42	2.86	1.40	1.91

The discrepancies between duplicate samples are believed to be due to their having received unequal amounts of sunlight, as it was necessary to place the flasks in a crystallizing dish to prevent their blowing away, and late in the afternoon those outside were in the sun longer than the others.

Another test was then started with approximately 10-g samples, the flasks being weighed at intervals. After each weighing the flasks which showed the least gain were placed so as to receive the maximum of sunlight. For this reason the last figures given in the next table are more concordant than they would otherwise have been.

Sample	B	B	C	C	D	D
Weight of oil..................	10.002	10.012	10.025	10.023	10.023	10.003
Total gain after—						
31 days (g)..............	0.176	0.152	0.187	0.183	0.154	0.139
46 days (g)..............	0.192	0.174	0.215	0.207	0.176	0.159
80 days (g)..............	0.233	0.223	0.274	0.278	0.221	0.201
110 days (g)..............	0.277	0.263	0.327	0.340	0.274	0.243
132 days (g)..............	0.290	0.289	0.358	0.369	0.297	0.268

That the increase in weight is somewhat influenced by the temperature, and is not entirely due to rays of short wave length, seems clear from the results obtained when two lots of oil B were exposed in very shallow dishes made by cutting off the bottoms of two beakers of the same diameter. One was covered with a thick watch glass. The other was uncovered, and was so shallow that hardly any light passed through glass before falling on the oil. The results follow:

Dish	Uncovered	Covered
Weight of oil	10.001	10.001
Gain after 6 hours bright, sun (g)	0.0354	0.0354
Further gain after 6 hours, bright sun	0.0183	0.0198
Further gain after 6 hours, bright sun	0.0154	0.0179
Further gain after 6 hours, partly cloudy	0.0085	0.0094
Further gain after 4 hours, partly cloudy	0.0050	0.0061
Further gain after 6 hours, dull one-half of time	0.0059	0.0068
Further gain after 6 hours, dull one-third of time	0.0063	0.0071
Further gain after 6 hours, dull one-half of time	0.0049	0.0065
Total gain (g)	0.0997	0.1090

In the cool, windy weather then prevailing, the oil in the covered dish must have been warmer than that in the uncovered one. On the first five days the dishes rested on white paper. This was replaced by black paper on the last three days, but only a slight change in the results was noticed. The increasing opacity of the oil owing to the formation of insoluble matter and the increasing saturation with oxygen would both tend to mask any effect due to a slight rise in temperature. Traces of precipitate were noticed at the end of the first six hours.

The above results show only that the temperature exerts some influence, but do not enable one to decide whether or not the part played by light is of greater or less importance. We then heated 10.014 g of the oil in a flask with ground-in stopper, connected with an air-purifying train and a calcium chloride tube, followed by a flask containing baryta water. The flask was then placed in a water bath made of a porcelain beaker surrounded by a sheet-iron cylinder. The top was covered with a perforated metal plate. The projecting neck of the flask was wrapped in cloth to exclude light. Under these conditions the oil was heated in a very slow current of dry air to 40°, for 16 hours in all, on three consecutive days. So little barium carbonate was precipitated that the heating was continued for six and a half hours on each of two consecutive working days, to 50°, 60°, 70°, 80°, and 90°. Even then it was not thought worth while to determine the small amount of carbon dioxide precipitated as barium carbonate. The calcium chloride tube showed a gain of 0.0156 g, while the flask, instead of gaining in weight, lost 0.0030 g.

More of the same oil, 11.274 g, was exposed outside the window for 18 hours, the temperature being kept down by surrounding the flask with ice and water. There was a gain in weight of 0.0069 g, though for at least five hours the sky was cloudy. The ice was then replaced by water kept between 12° and 18°. The gain in 23 hours in all on four consecutive days was 0.0282 g more. A slight precipitate formed.

These results make it evident that the action of light has a far greater effect than raising the temperature to 90°.

The observed increase in the weight does not truly represent the amount of oxygen involved, for carbon dioxide, water and volatile organic matter are lost. Twenty-five g of oil B were exposed in a flask having a glass stopper with sealed-in tubes so that a slow current of purified air could be passed over the surface of the oil, carrying the carbon dioxide into baryta water. In seven days, only three of which were sunny, 0.0249 g of carbon dioxide was found. On exposing the same sample for seven days longer, about four and a half of which were sunny, there was a further formation of 0.0223 g of carbon dioxide.

In a final experiment, the oil was exposed in an Erlenmeyer flask with glass stopper and delivery tubes. The water formed was carried, by a slow current of dry air passing over the surface of the oil, into a calcium chloride tube and finally weighed. It was noticed that the calcium chloride where the air entered was stained yellow, and that there was a whitish coating on the inside of the tube leading in through the window from the flask. Evidently some organic matter was given off. The carbon dioxide was absorbed in baryta water as before, was finally set free by dilute hydrochloric acid, absorbed in a potash bulb, and weighed. The change in weight of the oil was also determined, as well as the amount of the insoluble oxidation product. The following data were obtained after 22 days' constant exposure on the window sill:

	Per cent
Gain in weight of oil	1.83
Water formed (corr. for H_2O in oil)	0.89
Carbon dioxide	0.37
Total	3.09
Oxidation product	1.47

The figures for water and gain in weight of the oil are slightly in error on account of the volatile oily matter mentioned. However, the total of 3.09 per cent agrees closely with the figure 2.89 per cent, obtained by adding the gain in weight of the oil to the oxygen in the carbon dioxide and water found.

The "insoluble" oxidation product dissolves to only a slight extent in ligroin. It is readily filtered on a Gooch crucible, and when washed with ligroin and dried is a light brown powder. It dissolves in strong alcohol and more easily in dilute alcoholic potash. All attempts to crystallize it and to obtain a crystalline potassium salt were fruitless.

The amount found evidently accounts for only a small part of the 1.83 per cent of oxygen taken up by the oil. The following analyses show that a large part of it remains in solution in the oil, or that most of the oil is too slightly oxidized to form the insoluble product.

	C		H		O	
Original oil	86.40	86.34	13.83	13.63		
Oxidation product	72.87	72.58	7.83	7.81	19.30	19.61
Oil filtered off	84.55	84.44	13.45	13.38	2.00	2.18

To determine possible changes in the acidity of the oils, 20-g samples of each were exposed, in duplicate, for 23 days. After diluting with benzene, they were titrated with N/10 alkali, using phenolphthalein as indicator. The results are calculated as percentages of oleic acid.

Sample	B	B	C	C	D	D
Original acidity	0.08	0.08	0.03	0.03	0.07	0.07
Acidity after exposure	3.66	3.75	3.29	3.30	3.00	....

Attempts to obtain concordant figures for the permanganate value of the oils were fruitless, as the permanganate was decomposed catalytically, no true end-point being obtained. The oils were shaken with dilute sulphuric acid and heated on the steam bath, standardized permanganate being added from time to time. Apparently the temperature was too high, for it has been shown quite recently by Sarkar and Dutta[20] that at or above 81°, permanganate is decomposed by manganous sulphate, with formation of manganese peroxide, even in the presence of considerable sulphuric acid. A large amount of peroxide was formed in the attempted oil titrations.

WASHINGTON, September 29, 1910.

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[20] Z. anorg. Chem., **67**, 225; 1910.

THE VISIBILITY OF RADIATION. A RECALCULATION OF KÖNIG'S DATA

By P. G. Nutting

Radiation of wave length .61μ (orange red) must be twice as intense as radiation of wave length .54μ in the green to produce the same luminous impression. Similarly radiation in the red at .65μ or in the blue at .47μ must be ten times as intense to produce the same illumination as in the green. By determining the intensities of radiation necessary to produce equal luminous sensations for a number of wave lengths, a complete curve may be obtained having a single maximum in the green and sloping off toward the extreme red and violet. This curve gives the *visibility* of radiation of the various wave lengths.

König investigated the visibility of radiation for his own eye, a normal trichomat, for nine different luminous intensities ranging from the threshold of vision up to about 600 meter-candles per sq. mm of pupil opening. Using a triplex gas flame as a source and a modified prism spectrophotometer, he started with a given intensity in the green at .535 and worked both ways in the spectrum, observing how much the collimater slit had to be opened in order to produce the same luminous sensation as in the green. His observed relative slit widths are given in Table I.

König obtained the spectral energy curve of his gas flame source from Langley and multiplying the above equivalent slit widths by the relative (to 535) spectral energy, took the reciprocal as "Helligkeitswerthe der Energie." These values were recalculated and reduced to maximum ordinate unity to illustrate visibility in the author's paper on the Luminous Equivalent of Radiation.

TABLE I

König's Data on Visibility[1]—Relative Slit Widths

Intensity Steps	T	A	B	C	D	E	F	G	H
Int. (m. c./mm² pupil)	.00024	.00225	.0360	.575	2.30	9.22	36.9	147.6	590.4
Ratio to Preceding Step		9.38	16	16	4	4	4	4	4
Wave Length	**Equivalent Slit Widths**								
670	296.1	189.0	29.08	14.53	4.56	1.955	1.403	1.23	1.17
650	178.3	87.6	13.9	5.98	1.95	0.991	0.667	0.547	0.420
625	34.8	20.55	6.20	2.93	1.004	0.497	0.392	0.307	0.289
605	12.1	8.60	4.29	2.073	0.869	0.451	0.321	0.289	0.274
590	5.65	4.29	2.75	1.86	0.787	0.523	0.376	0.346	0.330
575	2.76	2.00	1.68	1.42	0.868	0.568	0.449	0.459	0.424
655	1.40	1.232	1.10	1.037	0.876	0.702	0.621	0.603	0.590
535	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
520	1.07	1.09	1.12	1.16	1.40	1.71	1.76	1.77	1.80
505	1.54	1.58	1.59	1.81	2.30	2.78	3.75	4.06	4.46
490	2.34	3.00	3.06	3.33	4.93	7.97	8.91	9.53	10.06
470	5.92	6.49	7.22	7.75	11.0	20.7	22.9	26.6	....
450	19.21	21.5	20.95	24.2	40.7	57.3	62.9	....	....
430	131.6	115.4	85.9	119.2	138.	151.	....	....	....

[1] A König, Helmholtz Festgrüss, Beit. Z, Psych. u. Physiol. d. Sinnesorgane, Hamburg and Leipzig, 1891, pp. 309–388: Verh. d. Physik. Ges., Berlin, **11**, pp. 10–13, 1892: Gessammelte Abhandlungen, Leipzig, 903, pp. 244–213.

König's slit width data are free from objection, but some of his own and the author's[2] deductions from them are wrong. Visibility is the ratio of luminous intensity to energy intensity at each wave length, $V = L/E$. So that to obtain the visibility from constant luminosity data like König's, the relative amounts of energy entering the slit must be known in each case. This energy is the product of three factors—slit width, spectral energy of the source, and relative dispersion. König's original paper (Beit. Sinn. Org.) leaves one with the impression that the prismatic correction was applied, although his prismatic dispersion was not given. Dr. Ives kindly called the author's attention to the fact that this correction had not been made and that König's dispersion curve had later been published (Ges. Abh. Barth,

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[2] The Luminous Equivalent of Radiation, this Bulletin, **5**, pp. 261, 308; 1908.

1903). Since these visibility curves are of wide usefulness in spectrophotometry and problems in illumination, they have all to be recalculated to include the correction for variable prismatic dispersion.

In the following table are given for each wave length first the relative spectral energy, the dispersion correction, and the product of these:

TABLE II

Wave Length	Spectral Energy (Relative)	Prismatic Dispersion (Relative)	Energy Divided by Dispersion
670	13.0	0.649	20.1
650	8.88	0.718	12.38
625	5.38	0.817	6.60
605	3.99	0.909	4.40
590	2.97	0.980	3.03
575	2.27	1.067	2.13
555	1.48	1.222	1.210
535	1.00	1.402	0.712
520	0.720	1.554	0.465
505	0.488	1.730	0.282
490	0.370	1.919	0.193
470	0.251	2.185	0.115
450	0.169	2.462	0.069
430	0.114	2.775	0.041

In obtaining the visibility data of the final table below, the slit widths of the first table were multiplied by the numbers in the last column above. The reciprocals of these products give curves which, when reduced to maximum ordinate unity, are visibilities.

The most marked effect on the visibility curves of the correction for variable dispersion is the shift in the positions of the maxima from .565 to .544μ at high intensities and from .511 to .503μ at the threshold limen (Step T). They are but little affected in width or in general form.

TABLE III

Visibility Reduced Data

	T	A	B	C	D	E	F	G	H
430	.081	.093	.127	.128	.114	.114	....	....	......
450	.33	.30	.29	.31	.23	.175	.16	....	......
470	.63	.59	.54	.58	.51	.29	.26	.23	......
490	.96	(.89)	(.76)	(.89)	(.83)	.50	.45	.38	.35
505	1.00	1.00	1.00	1.00	.99	(.76)	.66	.61	.54
520	.88	.86	.86	.94	.99	(.85)	.85	.85	.82
505	.61	.62	.63	.72	.91	(.98)	.98	.99	.98
555	.26	.30	.34	.41	.62	.84	.93	.97	.98
575	.074	.102	.122	.168	(.39)	(.63)	(.76)	(.82)	(.84)
590	.025	.034	.054	.091	.27	.49	.61	.68	.69
605	.008	.012	.024	.056	.173	.35	(.45)	.54	.55
625	.004	.004	.011	.027	.098	.20	.27	.35	.35
650	.000	.000	.003	.007	.025	.060	.085	.122	.133
670	.000	.000	.001	.002	.007	.017	.025	.030	.030
λ max	.503	.504	.504	.508	.513	.530	.541	.543	.544

WASHINGTON, October 1, 1910.

A PHOTOMETRIC ATTACHMENT FOR SPECTROSCOPES

By P. G. Nutting

The instrument here described was designed for spectrophotometric work and with three ends in view: (1) High sensibility, (2) economy of light, and (3) variable dispersion. Tests of a sample instrument constructed by Fuess show that the sensibility has been pushed to the limit of sensibility (1.5 per cent) of the eye, while the light economy is quite satisfactory and the dispersion that of any spectroscope to which it is attached. No trace of stray light can be detected in the new instrument and the single face on which dirt could cause stray light is entirely inclosed. There is a slight correction to the scale reading, but this is less than 2 per cent at its maximum.

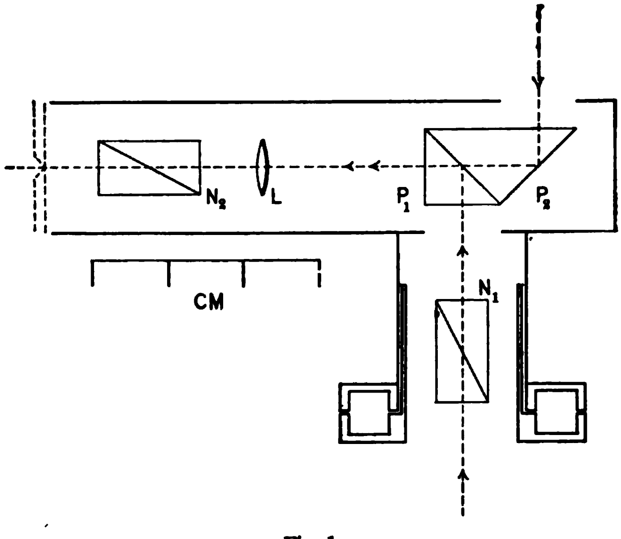

Fig. 1

The attachment consists of two reflecting prisms, P_1 and P_2, two Glan-Thompson nicols N_1 and N_2 and a lens arranged as shown in the figure. The whole is attached to the slit of any spectroscope, for example one of the Hilger "wave length" type. The essential feature is that a real image of the photometric surface (the common surface of the two reflecting prisms) is thrown on the slit by an achromatic lens and may thus be brought into the plane of the slit. The two beams of light to be compared, one passing through and the other reflected from the photometric surface, are brought to equality by rotating the nicol N_1. The photometric surface is alternately silvered and clear, the silver strips being 0.25 mm wide and separated by clear strips equal in width to the silvered strips.

The combination of reflecting prisms was suggested by and is similar to that used by Dr. H. E. Ives[1] in his new spectrophotometer, but in his instrument the photometric surface is silvered halfway across instead of in fine strips.

Both beams are polarized by reflection and the instrument was carefully tested for departures from the cosine square law of intensities. First the reflecting system was removed and the elliptical polarization (change of phase and rotation) produced by reflection on each of the reflecting surfaces determined for 45° incidence and 45° azimuth. The second test was by means of an auxiliary nicol placed before the free opening so that both beams were polarized before reflection. The third test was with rotating sectored disks of fixed known openings mounted before the free opening of the instrument. In this last test the sources were seasoned glow lamps operated in series with a rheostat on a storage battery circuit. The distances of these lamps were adjusted to equality of illumination with the 180° disk moving and the nicol at 0°. Then other sectors were substituted for the 180° sector and the readings of the nicol compared with their theoretical values deduced from the sector openings. The corrections were nowhere in excess of 2 per cent and of such sign as to indicate that they were in large part due to accidental errors.

The sensibility of the instrument was tested by rotating a parallel glass plate of known index in the path of one beam and by repeating readings. Sensibilities varying from 0.015 to 0.018 were recorded.

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[1] Phys. Rev., **30**, p. 450; 1910.

The excellent showing made by the instrument is due in some measure to the excellent workmanship displayed in the construction of its optical parts. But two minor improvements suggest themselves; that the position of the lens be made adjustable from without and that the balancing nicol N_1 be provided with a larger (10 cm) divided circle to permit of more precise readings.

WASHINGTON, October 1, 1910.

SELECTIVE RADIATION FROM VARIOUS SUBSTANCES, III

By W. W. Coblentz

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I. INTRODUCTION

The present investigation is the beginning of an attempt to supply a long-felt need of an accurate knowledge of the spectral energy distribution, of some standard sources of light, in the visible and in the ultra-violet parts of the spectrum. The problem is a difficult one and heretofore has never been given thorough attention. Once the spectral energy distribution of a standard source of illumination is accurately known, it is possible to obtain the spectral energy distribution of other weaker sources of radiation by indirect methods, such as by spectrophotography or spectrophotometry. The standard sources which are the most easily reproduced are probably well seasoned incandescent lamps operated at a given efficiency. For ultra-violet radiation, however, they are quite impracticable on account of the absorption by the glass bulb which will not be sufficiently constant for different lamps. For ultra-violet work, flame standards seem the best adapted; and of these the acetylene flame seems the most useful on account of its high temperature. The effect of variations in atmospheric conditions will probably have but little influence on the spectral energy curve. The black body, while ideally more scientific, is hardly to be classed as a convenient standard. The carbon filament is a good substitute for the black body, since it shows but little selective radiation in the visible spectrum. In certain classes of work the ideal standard is the vacuum tube radiation. Here the radiation from the individual spectral lines is measured, and we are not concerned with spectral purity and other sources of error. The chief error lies in accurately measuring the energy, which is always very weak, especially in the violet.

In making preliminary experiments on the suitability of various sources of radiation as spectral energy standards several new phenomena were observed which required extensive investigation and which diverted the attention from the main problem. The results obtained are unique in themselves and are therefore published at this time, since the rest of the work has been postponed.

It will be shown on a subsequent page that, throughout the visible spectrum, the radiation from the acetylene flame is proportional, within the limits of experimental errors, to the thickness of the flame, so that the values of the spectral energy, given herewith, apply to a flame viewed flatwise or edgewise. This is not true of the infra-red spectral energy curves. Here the emissivity is no longer a simple function of the thickness of the radiating layer, and hence can not be considered a reference standard without specifying the manner in which the flame is used.

II. APPARATUS AND METHODS

1. THE SPECTROMETER

For investigating the infra-red spectrum a vacuum bolometer, a mirror spectrometer, and a fluorite prism were used. The essential features of this apparatus have been described in previous communications.

For investigating the ultra-violet and the visible spectrum, all of the apparatus was of special construction. The spectrometer was of special design, and made in the instrument shop of the Bureau. Not only were short focus lenses of large aperture provided, but the collimator tubes were also designed so as to utilize all the light arriving at the viewing end and to avoid reflected light.

The optical parts consisted simply of two plano-convex quartz lenses 6 cm in diameter and 18 cm focal length, and a large 60° quartz prism. For the visible spectrum triple achromatic glass lenses have been provided. Quartz is transparent to about $.25\mu$, hence the only loss is due to reflection. A light flint-glass prism was also employed as a check on the work. The dispersion was twice as great as in the quartz prism, which reduced the intensity of illumination. Hence the observations are of little value in the ultra-violet, where (at $.42\mu$) the absorption begins to be quite large.

The fewness of the reflecting surfaces reduced the energy losses by reflection. It will be noticed presently that the "scattered" light in the system is very uniformly distributed over the field. Hence while not negligible in the case of an intense source of radiation such as the Nernst glower, this diffuse light simply increases the observed radiation by a fixed amount throughout the entire spectrum. Of course, for a small angular distance from the normal, as obtains in the present experiments, the scattered radiation should be uniformly distributed, but heretofore no very definite experiments have been published to give the desired information.

From the observations of Rosenmuller[1] it appears that the actual loss of light in such an instrument is insignificant out into the extreme violet. For radiometric work this correction would have but little significance and in the present work no correction has been applied.

The collimator tube was provided with an accurately divided scale, which permitted setting the radiation meter in accurate focus at different parts of the spectrum. This scale was calibrated for proper focal lengths by means of the helium lines, which also served as a calibration of the prism. The change in focal length from .35μ to .75μ was about 15 mm, and at each spectrometer setting the instrument was set to accurate focus as determined from a calibration curve of the scale on the collimator tube. For the region from the yellow to the ultra-violet, however, where the dispersion is large, the matter of accurate focus was unimportant, as was found by actual observation.

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[1] Rosenmuller, Ann. der Phys., **29**, p. 355; 1909.

The spectral lines are of course slightly curved in such an instrument. The slit which covered the thermopile was therefore made of thin sheet copper cut so as to exactly fit the curvature of the spectral lines.

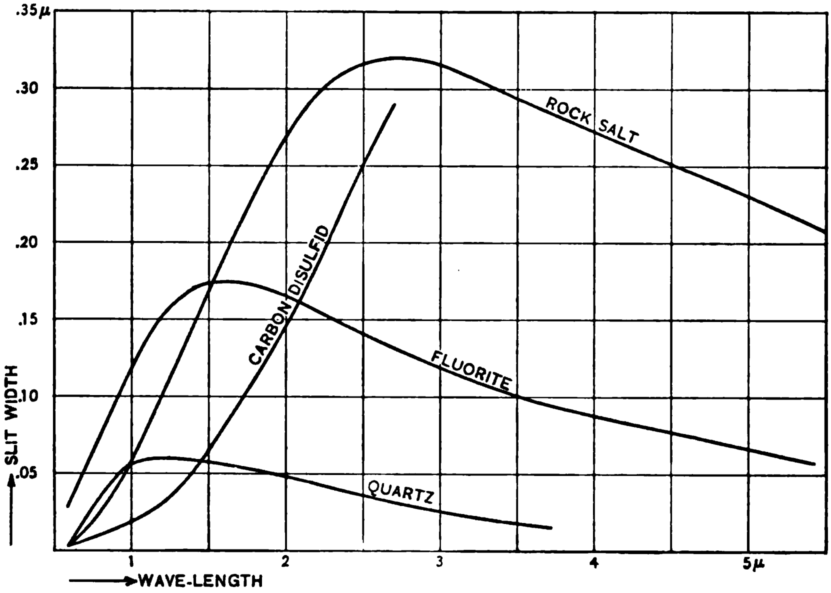

Fig. 1

2. COMPARISON OF DISPERSION OF PRISMS

It is of interest to notice the dispersion of various prisms in different parts of the spectrum. In fig. 1 is shown the width that a bolometer, having an angular aperture of 4′ arc, subtends in wave lengths (the "slit width") in different parts of the spectrum when using different prisms having the same angle—60°. These curves show that a carbon disulfid prism is the best for the region to 1.4μ. For most purposes quartz is the best.

In the present work the spectrometer slits were 0.6 mm wide, or about 10 minutes in arc. Even with this wide slit the actual width, subtended in wave lengths, is far less than for similar work in the infra-red, where even greater exactness is desired than in the present investigation. The slit-width correction, i. e., the factors for reducing the prismatic spectrum into the normal spectrum, were obtained from the curve of refracting indices and minimum deviation settings, and also by direct calibration of the prism by means of the helium lines. The values derived by these two methods agreed exactly throughout the whole range, except beyond .69μ, where they began to diverge. From .69 to .75μ the factors determined from the experimental calibration curve were therefore used. This divergence at .75μ is due in part to the fact that the dispersion curve of quartz has a point of inflection in this region of the spectrum, which makes it difficult to determine the slit-width factors with great exactness.

3. THE RADIOMETERS

A special Rubens thermopile[2] of 20 elements of iron and constantan and a new radiomicrometer were provided for this work. The thermopile wires were only .07 mm in diameter and the total resistance was 9.5 ohms. Wires of this fineness rust off very rapidly unless protected. They are therefore given a thin coat of shellac, which is baked. Because of this defect it seems advisable to use copper instead of iron in this form of pile. The thermoelectric power of copper-constantan is not very markedly different from the iron-constantan. The junctions are then painted with a mixture of lampblack and chemically precipitated platinum black, the brush used being an end of a silk thread. This thermopile was entirely free from the usual drift observed in the heavier type of instrument, and it came to temperature equilibrium in far less time than the actual period of the galvanometer. The latter has also been described. On account of the great light-gathering power of the spectrometer, a high galvanometer sensitiveness was not required, and it was generally used on 2.5 seconds single swing, which corresponded to about $i = 2 \times 10^{-10}$ amp. for a scale at 1 meter.

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[2] This Bulletin, **4**, p. 391; 1907.

Magnetic and thermal disturbances were inappreciable. In fact, with this apparatus far less difficulties were experienced than in the general infra-red investigations, which is just the opposite from what was expected before undertaking the work. To be able to make a reading in 5 seconds instead of 5 to 10 minutes, as was necessary heretofore, is an important item, especially when examining an open flame subject to various fluctuations in the surrounding conditions.

The thermopile was mounted in a heavy metal case, which was rigidly attached to the collimator arm. It was found that the eyepiece at the rear did not permit setting the thermopile slit upon a spectral line with as high degree of accuracy as was desired. Hence, after the completion of the focal length and the prism calibration the eyepiece was removed. This space was inclosed with black felt, which absorbed the radiation passing by the thermojunctions, and the adjustment of the thermopile slit (the so-called zero setting) was made by viewing it at an angle from the front. Using the intense yellow helium line as a reference point, there was no difficulty in testing this adjustment of the thermopile slit in the spectrum.

A new form of suspension was made for the radiomicrometer,[3] previously described, but on account of its inconvenience and because of the high sensitivity of the thermopile it was not put to extensive use. It has given such satisfaction in other work, however, that it seems worth while to describe it. The suspension, Fig. 2, consists of two junctions of bismuth and silver, with a copper loop, and it was made linear for spectral radiation work. It was found that by dropping the molten bismuth from a height of about 1 m it would spatter out into a thin, well-annealed plate, which could then be rolled to .02 to .04 mm thickness. The dimensions of the present junction were: Bi = 8 x 1 x .03 mm; Ag = 3 x 1 x .01 mm, and copper wire .08 mm in diameter. The central active junctions were painted on one side with a mixture of platinum black and lampblack, with a trace of shellac in alcohol. The window covering the junctions consisted of a film of glass blown so thin that it showed interference colors. Such a film absorbs but little in the spectrum, except at 8 to 9μ.[4]

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[3] This Bulletin, **2**, p. 479; 1907.

For a candle at 3.1 meter and scale at 1 m, with all extraneous light excluded except that which passed through a long blackened tube, the deflection was 22 cm (for a single swing of 25 sec.) or more than 200 cm at 1 meter. For a single swing of 10 sec. the deflection was at least 50 cm. It is therefore apparent that this form of junction is as sensitive as any heretofore described. The weight of the complete suspension was a little less than 10 milligrams. The sensitiveness of this suspension was not very much greater than that of a similar suspension having but a single thermojunction, which is in accordance with the theory.

From the fact that the galvanometer did not have to be forced to its highest sensitivity it is not to be inferred that spectral energy curves in the visible spectrum can be easily observed with ordinary apparatus. The intensity in the yellow is about 400 times and in the red (.725μ) it is about 3000 times that at .38μ. On the large mirror spectrometer, using the small fluorite prism previously described, the Nernst glower gave a deflection of about 2000 cm at the point of maximum emission. With 6 times the light-gathering power, which obtains in this instrument, the deflections would have been 12 000 cm at the point of maximum emission. With the present instrument, using a quartz prism, the intensity of maximum emission (at 1.35μ) of the Nernst glower would be about 90 000 times that at .38μ.

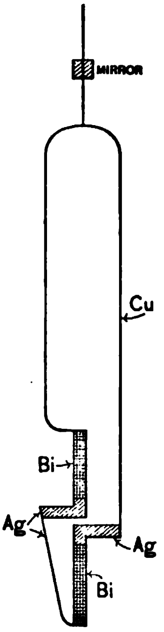

Fig. 2

4. THE ROTATING SECTORED DISK

With galvanometer deflections ranging from 70 cm in the yellow to 400 cm in the red it was necessary to provide apparatus to reduce the intensities to a measurable value. This could be done either by throwing resistance in series with the galvanometer, or by reducing the incident light with a convenient form of rotating sectored disk. The present sectored disk consists of eleven series of openings at 90° from each other, each opening being 16 mm long, the respective angles being 2°, 3°, 4°, 6°, 8°, 10°, 12°, 15°, 20°, 30°, and 45°. This gives reduction factors ranging from ½ to $^1/_{45}$ the original intensity, which seemed sufficient as a first experiment. This disk, although 41 cm in diameter, and made of copper about 1 mm in thickness, with aluminum bracing arms 10 cm long and about 5 mm thick, has proven to be thoroughly rigid and free from lateral vibration when in rapid motion. The thickness of the whole framework was kept small, 1 cm, to reduce the air path in infra-red radiation work. The essential parts of this form of disk are (1) a large disk with numerous openings (nothing particularly new about it) which reduce the intensity by an accurate amount at each step; (2) a motor rigidly attached to the frame supporting the disk, and moving with it; (3) a slotted base plate, supporting this framework, and provided with a rack and pinion to move this frame, containing the disk and motor, back and forth in front of the spectrometer slit. A long rod is provided to operate the pinion from a distance. The whole is shown, without details, in Fig. 3 and needs no explanation. From a mechanical point of view it might be better to have the large angular openings nearer the rim, thus reducing the weight, and to increase the accuracy in the small angular openings at the center by using, for example, two 4° openings situated at 180° instead of four 2° openings situated at 90° from each other. This would permit larger angular openings, although for radiometric work a reduction factor of less than ½ is of little use. Openings both larger and smaller are possible, but previous experience showed that the aforesaid factors would be the most useful as a preliminary attempt. Provision has, of course, been made for substituting another disk with different openings. This experiment shows that still larger disks can be operated without vibration. Of course, where only spectroradiometric work is contemplated with a slit of less than 1 mm wide, more steps can be put in the smaller disk. The present instrument is also useful for total radiation work. The definite openings make errors impossible in setting them before the slit, and they fill all the requirements in

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[4] See Investigations of Infra-red Spectra, Vol. II, p. 65; 1906.

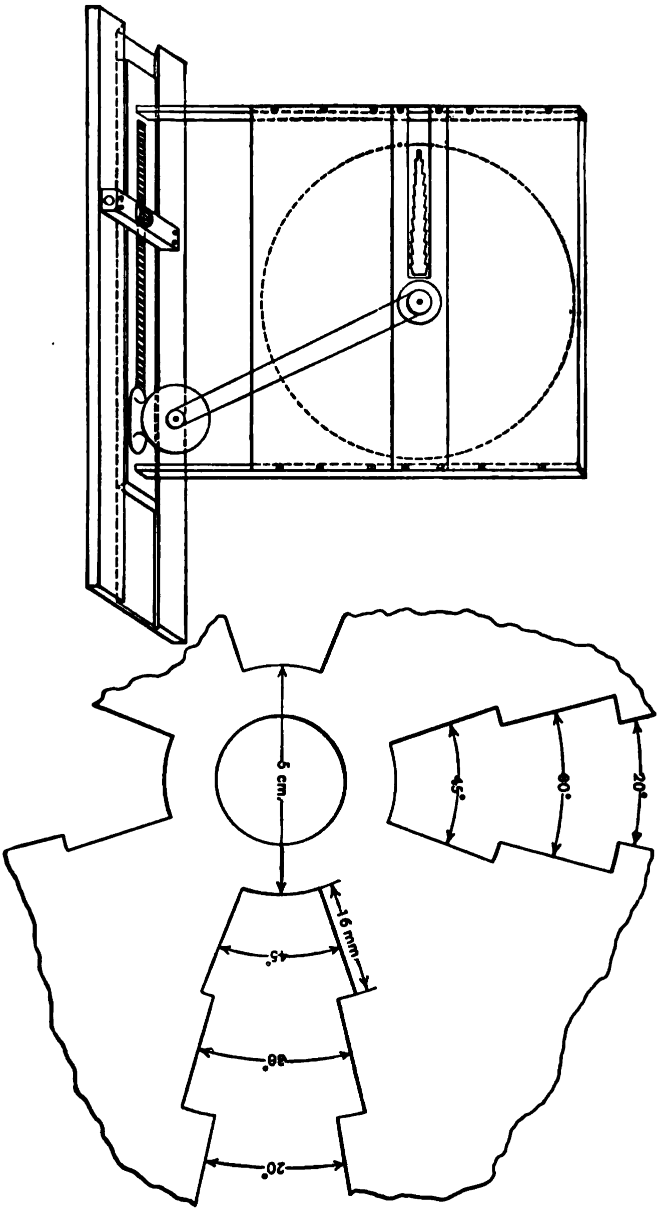

Fig. 3

radiometric work where it is necessary to reduce the radiation by a definite amount. A uniformly decreasing angular opening (instead of step-wise as in this case) is easier to construct and would be useful, also, in spectrophotometric work, such as the instrument recently described by Hyde.[5] But such extreme care is necessary in adjusting and in making settings before the spectrometer slit with the latter form, that at the time when the design of a rotating sector was undertaken no thought was given to the development of such an instrument. These two types of rotating sectors are excellent examples of what may be independently developed by two investigators to fulfill their individual needs.

5. ACCURACY ATTAINABLE

The fact that the galvanometer could be used on a very short period made it an easy matter to investigate the visible spectrum. A casual examination of the records shows that in the yellow and in the red where the deflections (actual or reduced) were from 10 to 20 cm, the individual readings vary by .3 to .5 mm from the mean, or one part in 200 to 400. The intensity of the radiation, falling on the front part of the thermopile case which consisted of a double-walled copper shield with a slit in it to permit the radiation falling upon the active junctions, caused a slight unsteadiness of the zero reading, and hence lowered the accuracy attainable. In the blue and green where the deflections were from 5 to 10 cm the zero reading was not affected by the excessive heating and the individual readings vary by .2 to .3 mm (for example 5.83; 5.82; 5.82; 5.84; 585; 5.83 cm), or one part in 200. In the extreme violet and in the ultra-violet (except for the Nernst glower) where the deflections were only from 3 to 5 mm, the accuracy attainable was only from 1 part in 10 to 1 part in 50. In case of the Nernst glower, in the extreme ultra-violet, and in the stray light measurements, where the deflections were 15 mm, the variations from the mean (which includes fluctuations in the glower due to air currents) were less than .5 mm or about 3 per cent. On the whole, this refinement is of minor importance, for the interest lies in the general trend of the energy curve from the extreme ultra-violet into the infra-red. It may be added, in conclusion, that a small fluctuation of .1 to .2 volts, in incandescent lamps, although observable on the spectrophotometer, did not affect the observations by a perceptible amount, except in the case of the Nernst glower, in which a variation of 0.1 volt caused an appreciable variation in the emissivity in the yellow and especially in the red. All the lamps were operated from a storage battery, so that the voltage was easily held constant. The voltmeter was calibrated several times and found to be constant. The incandescent lamps were seasoned by the photometry division of this Bureau, and the voltages specified for obtaining a definite efficiency. For this purpose, a series of efficiency measurements (candlepower and watt-input) were made, varying from, say, 2.3 to 3.5 w. p. m. h. c, and a curve was drawn. from which the voltage could be read for the production of, say, 2.5 wpc.

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[5] Hyde, Phys. Rev., **31**, p. 183; 1910.

In conclusion, it seems desirable to emphasize the fact that the accuracy attainable in radiometric work is greatly influenced by weather conditions, just as in astronomical work. The present observations were made in the hottest summer months when the temperature within the observing room was closely the same as on the outside of the building. Even then cloudy, wind-free days were the best. In subsequent work, several months later, when it was more windy, and when the room temperature was different from the outside, the thermopile was more unsteady in its action. The galvanometer mirror would also fluctuate a little, due to air currents and probably also to changes in astatacism caused by a slight swaying of the building by strong gusts of wind, so that a precision of only 1 part in 100 to 200 was possible.

III. THE ACETYLENE FLAME

1. HISTORICAL

That particles of incandescent carbon in flames, and especially in incandescent lamp filaments of carbon, can have a sharp band of selective emission just beyond the visible (red) spectrum has always seemed to the writer to be doubtful. The properties of "soot" and "lamp black" are a high absorptivity in the visible spectrum which decreases rapidly as we go into the infra-red. The experiments of Ladenburg[6] on the incandescent particles in the acetylene flame show a similar property of a high absorption in the visible spectrum which decreases uniformly in the infra-red. In order to have a sharp band of selective emission the flame should show a band of strong, well-defined absorption in this same region. The curves of Ladenburg do not indicate such a condition. From all the experimental data now at hand one would expect a much higher emissivity in the blue, decreasing uniformly into the infra-red, just as obtains in the metals. That this is actually the case for acetylene was found by Dr. Burgess, who kindly made the measurements with an optical pyrometer.[7] The pyrometer showed an emissivity equivalent to a black body at a temperature of 1357° in the red, to 1450° in the green, and to 1475° in the blue, which is the order of the selective emission of metals. In view of the fact that, as will be noticed presently, the acetylene flame seems to show a slightly more transparent region in the violet, it would be interesting to have a comparison of this same region with a sensitive optical pyrometer.

Spectrophotometric intercomparisons of various flames and incandescent lamps seem to show a band of selective emission in the deep red.[8] The acetylene flame was used as a comparison standard. Because of its rapid change in absorptivity (and hence emissivity) in the region of $.75\mu$ (see Fig. 9), the slope of the spectral energy curve of acetylene is entirely different from that of an opaque solid, e. g., a carbon filament. Hence the curve of ratios of emissivities of these two substances assumes various forms (depending upon the temperature of the carbon filament) which, combined with errors due to stray light, lack of sensitivity of the eye, etc., give the appearance of a band of selective emission at $.72\mu$ when in reality the whole is due to a rapid variation in transparency[9] in the region of $.7$ to $.8\mu$.

The logical procedure is, of course, to compare such sources against a black body which can not emit selectivity in favor of some particular spectral region. About two years ago a preliminary spectrophotometric comparison was made of a carbon lamp and of an acetylene flame, with the radiation from a black body. At that time no permanent acetylene apparatus was at hand. A temporary generator and gasometer were constructed, with which acetylene was produced for two series of spectrophotometric comparisons, and for the pyrometric comparisons just mentioned. Because of the difficulty of operation and the lack of assistance further work was discontinued until the completion of the Bureau's permanent acetylene gas generating apparatus, which now consists of an automatic generator attachable to either a high or a low pressure gasometer.

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[6] Ladenburg, Phys. Zs., **7**, p. 697; 1906.

[7] This Bulletin, **5**, p. 364; Table III.

[8] Nichols, Phys. Rev., **13**, p. 65; 1901; Blaker, Phys. Rev., **13**, p. 345; 1901.

[9] This Bulletin, **5**, p. 376; 1909.

In the spectrophotometric measurements no selective emission was found in the carbon lamp; but the acetylene flame seemed to show selectivity in the deep red.[10]

From a recent study of the original observations it appears to the writer that the conclusions[11] of a true selective emission at .7μ was erroneous. The data then obtained, when properly interpreted, indicates a low emissivity in the region of .7μ. But the eye is not sufficiently sensitive to differences in intensity for frequencies beyond .7μ to put much reliance in these spectrophotometric observations. Moreover, from recent experiences with the spectrophotometer then used, the writer feels that even a substitution method of comparison may not eliminate all errors. In the apparatus used by us the photometric field is not evenly extinguished by the rotating sector (in this device the sector is stationary and the beam of light is rotated), the line of extinction being from the lower right-hand quadrant to the upper left-hand quadrant. In the extreme red the eye, therefore, unconsciously tends to wander from side to side and inconsistent settings result. In some recent spectrophotometric work consistent results were obtained only by fixing the eye on the central part of the photometric field. If the same conditions obtained in our acetylene comparisons, the apparent selectivity is easily explained. This same thing, however, should have also appeared in the spectrophotometric comparisons of the incandescent lamps. On a subsequent page it will be shown that the previous announcement[11] of a selective emission band at .72μ was based upon a misinterpretation of a peculiar depression in the spectrophotometric curves of acetylene (compared against a black body) which is not due to a true emission band, but is due to a rapid decrease in the absorptivity of the acetylene flame in this region of the spectrum. Suffice it to say that any selectivity of even a small part of that recorded by us spectrophotometrically could not have, as will be noticed presently, escaped detection radiometrically. The radiometric observations, at any spectrometer setting, are in agreement to at least 1 part in 200 and often to 1 part in 400 (the slight fluctuations in the galvanometer deflections being due to the unsteadiness of the acetylene flame) which accuracy can not be attained with a spectrophotometer, at least not in the extreme red end of the spectrum. As the one principally responsible for undertaking this work, the writer can but express his regrets that anyone should be misled into a discovery of selectivity[12] from the preliminary spectrophotometric data then obtained. Other data then at hand was overwhelmingly against our spectrophotometric results and with the new data, to be discussed presently, the writer feels no necessity for changing the views then expressed,[13] namely that the apparent spectrophotometric selectivity is not due to a true emission band, but is due to an increase in transparency of the acetylene flame in the infra-red. Previous observations on the distribution of energy in the spectrum of the acetylene flame were described by Stewart;[14] but the data is not applicable to the present question of a selective emission in the visible spectrum.

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[10] This Bulletin, **5**, p. 376; 1910.

[11] This Bulletin, **5**, pp. 349 and 376; 1910.

It is to be noticed that in the present experiments the light-gathering power of this instrument was six times that used in previous investigations of acetylene. The dispersion was also considerably greater than used heretofore, being almost five times as great when using the glass prism. Furthermore, there is no uncertain absorption due to silvered mirrors. The instrument was capable of collecting sufficient light and in producing a sufficiently long visible spectrum to make observation easy, accurate, and free from doubt. If a band of selective emission, of appreciable intensity, exists at .7μ, it must, therefore, be observable in the spectral radiation curve.

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[12] Hyde, Jour. Franklin Institute, **170**, p. 29; 1910.

[13] This Bulletin, **5**, p. 376; 1910.

[14] Stewart, Phys. Rev., **13**, p. 257; 1901; **16**, p. 123; 1902.

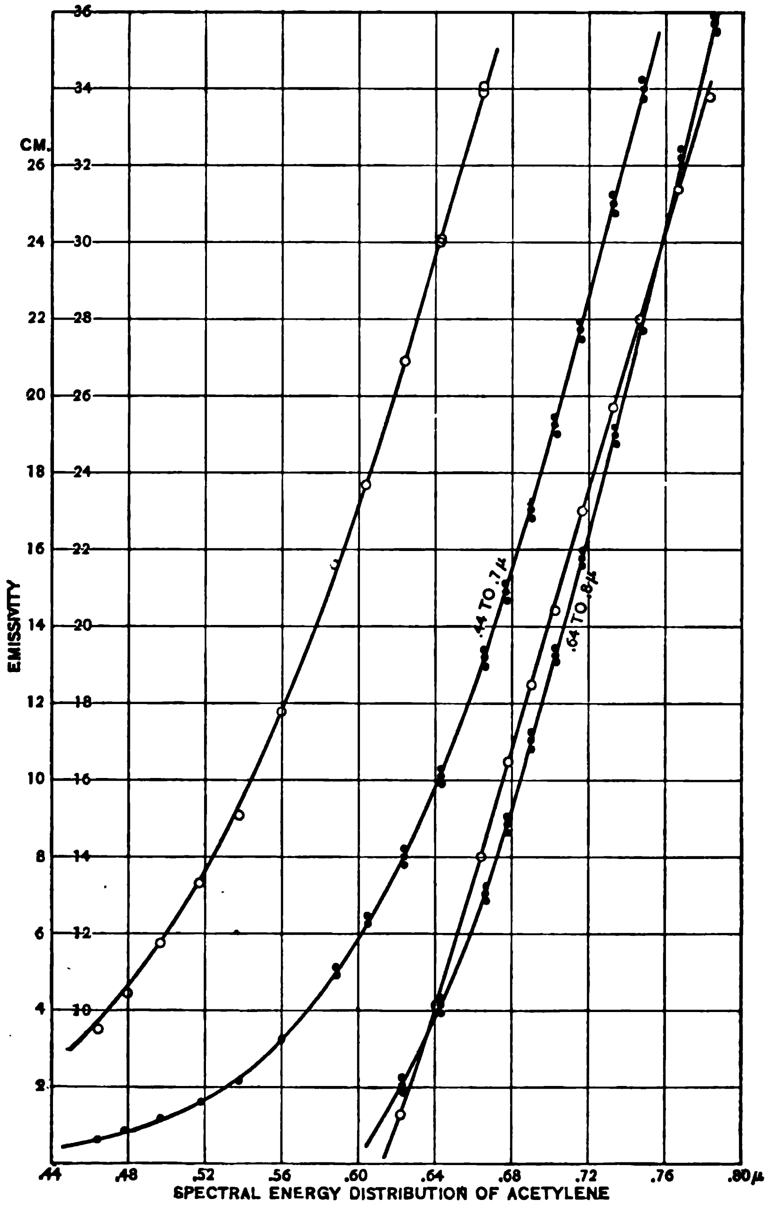
2. THE VISIBLE SPECTRUM

For the present investigation, the acetylene was produced by a commercial automatic generator. It was burned as it came from the gasometer, without additional drying, and hence was investigated as in previous experiments. For the flat flame, a Von Swarz "Perfection" acetylene burner was used. The rated capacity was ¾ cu. ft. per hour, operated on a pressure of 7 cm (2½ inches) of water. A lava tip of a "Naphey" burner was also used. This consumed ¼ cu. ft. per hour. It gave a cylindrical flame about 3 cm high. Spectral energy curves of these two flames were also obtained when burning under a gas pressure of 10 cm (4 inches) of water. It was found that the spectral energy curves of these two flames coincided exactly when operated under the same gas pressure. No data was obtained of the cylindrical acetylene flame when burning under 7 cm water pressure. The observations on the flat flame show that for the same intensity in the violet the intensity in the red is greater on the normal water pressure of 7 cm than on the higher pressure of 10 cm water. In view of the fact that the observations on the flat flame were made on different days with different adjustments of the flame before the spectrometer slit, further observations will be necessary to determine whether this is solely due to a variation in pressure.

In these three series of measurements, using the quartz prism, no selective emission (which should manifest itself as a hump at .7μ in the spectral energy curve), could be observed either in the prismatic or the normal spectral energy curve. As a further check on the accuracy, using a larger dispersion, the apparatus was readjusted and a light flint silicate prism substituted for the one of quartz. With this larger dispersion, using the rest of the apparatus as before, the galvanometer deflections were reduced to 5 cm in the yellow and a total deflection of 35 cm in the red. For accuracy in measuring the galvanometer deflections, all readings were reduced to about 15 cm, and, since the deflection could be read accurately to 0.3 mm, to 0.5 mm, a precision of 1 part in 300 to 400 would easily have been possible. But the flame was subject to fluctuations, due to air currents, of 1 to 2 mm (galvanometer deflection), so that this precision was considerably reduced. The results obtained on the flat flame are shown graphically in Fig. 4, in which the continuous lines (· · · ·) give the observations in the prismatic (glass) spectrum and the dotted lines (⊙ ⊙ ⊙ ⊙ ⊙) give this same data reduced to the (approximate) normal spectrum.

The normal spectral energy curve of the flat flame, obtained by using the quartz prism, coincides within 1 per cent throughout the whole length with the normal curves given in Fig. 4. This is an excellent test of the factors used in reducing the prismatic curves to the normal curve. No correction has been made for change in focal length which would increase the curvature in the red.

In the prismatic curves, Fig. 4, the three dots at each point of observation, for example at .7μ, indicate the maximum, the mean (of 10 to 15 observations), and the minimum deflections representing three series of observations made in rapid succession back and forth throughout the spectrum. The whole time consumed was less than two hours, with the barometer reading 755 mm and a relative humidity of about 69 to 70 per cent. No irregularity is observable in the energy curves, greater than that due to fluctuations in the flame, and it can safely be said that these curves show no band of selective emission, at .7μ to .72μ, in which the maximum rises as much as one per cent above the general trend of the spectral energy curve. The spectrophotometric data would indicate a protuberance at .70μ rising several centimeters above the general trend of the spectral energy curve. Furthermore, the spectral energy curves, obtained with this apparatus, of carbon filament lamps show no selective emission in this region. It is therefore an interesting question why the spectrophotometric intercomparisons of these two sources should indicate an abnormal emission beyond 0.7μ. The very marked difference of their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.68
.72
.76
.80μ
.44 TO .7μ
.64 TO .8μ
SPECTRAL ENERGY DISTRIBUTION OF ACETYLENE

Fig. 4

emissivities in the infra-red should produce a maximum in their ratios of intensities. This maximum for a 2.5 watt "Gem" carbon filament lies at about .55μ. See Figs. 6 and 8.

In Fig. 5, curve *a* shows the normal spectral energy curve of the acetylene flame, determined with the mirror spectrometer, fluorite prism, and vacuum bolometer. In order to obtain sufficient intensity, the flame was placed so that it radiated edgewise into the spectrobolometer. The curve has been corrected for absorption by the silver mirrors. The values obtained by Stewart, using a cylindrical flame, have been similarly corrected and reduced to a normal spectrum by means of the writer's slit width factors. The two curves coincide exactly throughout the whole visible spectrum. The lack of coincidence in the infra-red is no

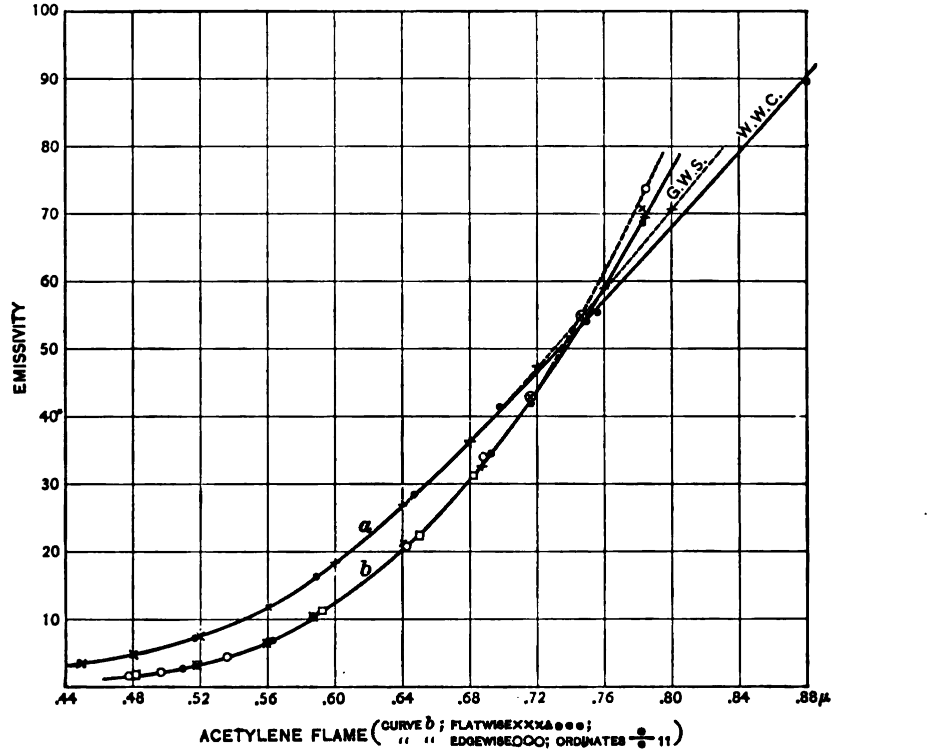


Fig. 5

doubt due to the difference in the effective thickness of the two flames, as will be noticed on a subsequent page. The values of the various emissivities (arbitrary units) of the normal spectral energy curve of acetylene are given in Table I. The values at .36μ to .52μ were obtained with the quartz lens spectrometer. They coincide exactly, over the common range from .44μ to .52μ, with the values obtained with the mirror spectrometer having three reflecting mirrors. Using five mirrors, instead of three, the spectral energy curve at .40μ to .44μ falls slightly below the values given in Table I. This is no doubt due to the lack of a proper correction for the absorption by the silver mirrors.

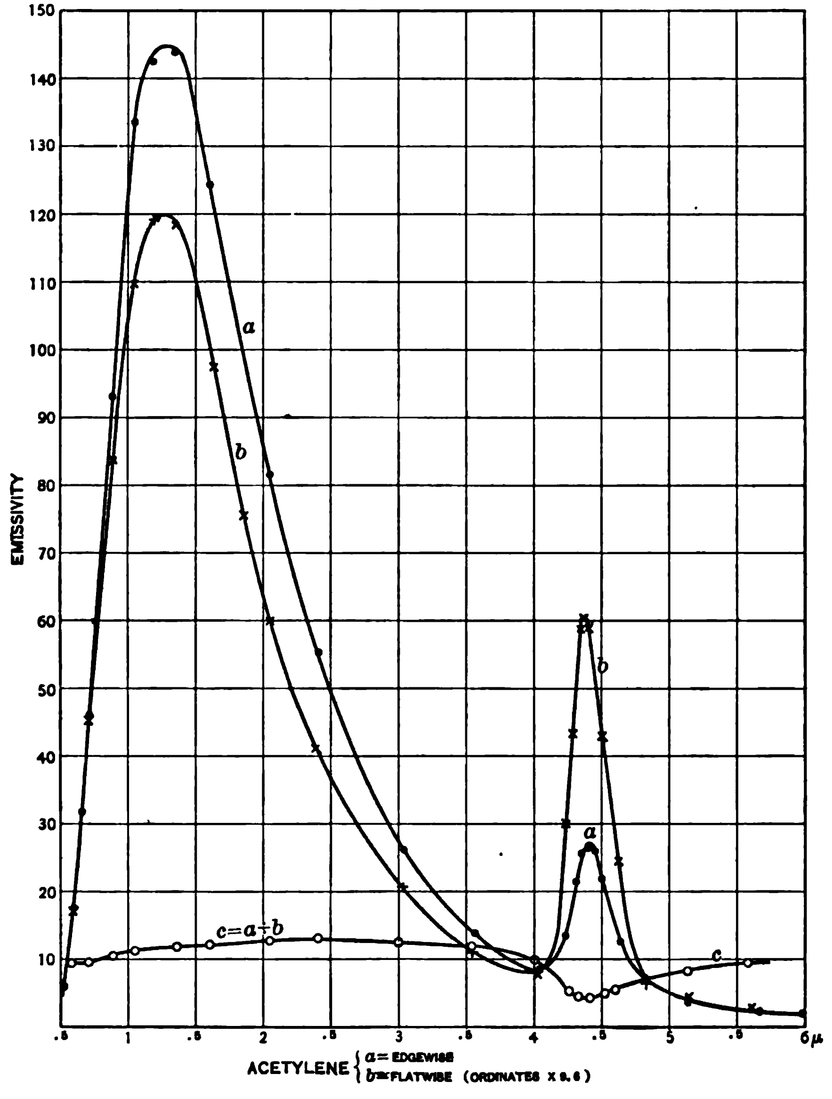
TABLE I

Wave Length in μ = .001 mm	Emissivity	Wave Length in μ = .001 mm	Emissivity
.36	3.5	.56	43.7
.38	4.4	.58	54.0
.40	5.8	.60	66.3
.42	7.2	.62	80.5
.44	9.7	.64	96.5
.46	12.5	.66	112.8
.48	16.5	.68	130.1
.50	21.7	.70	147.0
.52	27.6	.72	163.8
.54	34.8	.74	181.5

3. EMISSIVITY A FUNCTION OF THE THICKNESS OF THE RADIATING LAYER

The acetylene flame consists essentially of incandescent carbon particles in the process of combustion, suspended in the heated gases, CO_2 and H_2O, which are the combustion products of acetylene. The spectral energy curve therefore consists of a continuous spectrum due to the incandescent carbon particles superposed upon the composite emission spectrum of water vapor and carbon dioxide, which consists of strong emission bands, notably at 2.7μ and 4.4μ.

In order to be able to use the acetylene flame as a standard of reference in spectral radiation work, it is important to know how the emissivity varies with the thickness of the flame. That the thickness of the radiating layer has but slight if any effect on the shape of the (prismatic) energy curve in the visible spectrum is shown in Fig. 5, curve *b*, which gives the radiation from the flat side (xxx and · · · ·) and the edge (⊙ ⊙ ⊙) of the flame. In this experiment the acetylene flame, radiating edgewise into the spectrometer slit, illuminated a width of only about 1.5 cm of the glass prism, which was therefore entirely covered except about 1.5 cm of the central part of the face. In this manner, the flat side of the flame illuminated the same width as the flame turned edgewise. The expectation was to find a marked increase in the emissivity in the red when the flame was radiating edgewise into the spectroradiometer. The deflections were eleven times as large as those from the flat side of the flame, but when reduced to the same scale and plotted, as shown in curve *b* Fig. 5, they coincide throughout the whole range. In this experiment the radiation from the flat flame (xxxx) was first observed, then the flame was accurately adjusted edgewise (⊙ ⊙ ⊙ ⊙), and finally the observations were repeated on the flat flame (· · · · ·). The observations of the flame radiating edgewise were subject to greater variations (due to air drafts which deflected the flame from the 1.5 cm opening of the cover on the prism) than when observed flatwise, and, in all, less observations were made than for the curves in Fig. 4. Nevertheless, there is an exact coincidence of the three series, throughout the visible spectrum, showing the same relative emissivity when viewed flatwise as when viewed edgewise. This is probably to be expected in view of the fact that the variation in the absorptivity with thickness of the flame is not very marked in this spectral region. Moreover, in this spectral region the variation in absorptivity (emissivity) with the wavelength is not so marked as in the infra-red. In this same curve the observations marked with the rectangles (⊡ ⊡ ⊡ ⊡) were made with the same apparatus, and a flat flame, a month later when metereological conditions were different, and when the gas generator contained a fresh charge of carbide. The observations coincide exactly with those previously obtained.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a
b
b
a
c=a÷b
c
.5
1
.5
2
.5
3
.5
4
.5
5
.5
6μ
ACETYLENE { a= EDGEWISE
b= FLATWISE (ORDINATES X 9.6)

Fig. 6

In Fig. 6, curve *a* gives the normal infra-red spectral energy curve of the acetylene flame radiating edgewise into the silt, while curve *b* gives the energy curve of the same flame radiating flatwise into the spectrobolometer. In the latter all the observations were multiplied by the factor, 9.6, which produced an exact coincidence throughout the visible spectrum. In the infra-red there is a wide departure in the lack of coincidence of the two radiation curves. This is especially noticeable in the emission bands of carbon dioxide at 4.4μ. For the flat flame the ratio of the two maxima, $E\,(\max) : E\,(\lambda = 4.4\mu) = 2.05$ while in the flame radiating edgewise the ratio of $E\,(\max) : E\,(\lambda = 4.4\mu) = 5.5$. In other words, in viewing the flame flatwise the maximum emission of the CO_2 band is almost one-half as great as the point of maximum emission of the incandescent carbon particles, while in the flame viewed edgewise, the CO_2 band is only about one-fifth the maximum at 1.25μ.

Curve *c*, Fig. 6, gives the ratios of curve *a* to curve *b*, and it also shows that the emissivity of the CO_2 increased by a much smaller amount than did the emissivity of the incandescent carbon particles.

In Fig. 6 the relative areas of curves *a* and *b* are 88 to 74, which explains the wide variations in the various determinations of the luminous efficiency.

4. COMPARISON OF ACETYLENE FLAME AND A SOLID RADIATOR

The wide departure of the acetylene radiation from that of a black body is well illustrated in Fig. 6. For a black body (at the same temperature) there would not be a great depression in the spectral radiation curve, such as obtains in acetylene, between 1.5 and 4.4μ. This is illustrated in the following comparison of acetylene with a Nernst glower. While the Nernst glower at low temperatures [15] departs far from a black body in its radiation, it seemed of interest to compare the acetylene with it when the two were set to the same emissivity in the green. This was done by viewing the Nernst glower against the acetylene flame, using green glass, and varying the current through the glower until its color merged into that of the acetylene flame. The latter was viewed edgewise. The glower was a D. C. type 13 mm long, 1.03 mm diameter and rated at about 73 watts. To obtain a match with the acetylene, in the green, an energy input of only 36 watts was required. To the eye, of course, the glower is decidedly reddish in color, due to its greater emissivity in the red. This is well illustrated in Fig. 7, in which curve *a* gives the radiation from the Nernst glower and curve *b* gives the radiation from the acetylene

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[15] This Bulletin, 4, p. 540; 1908.

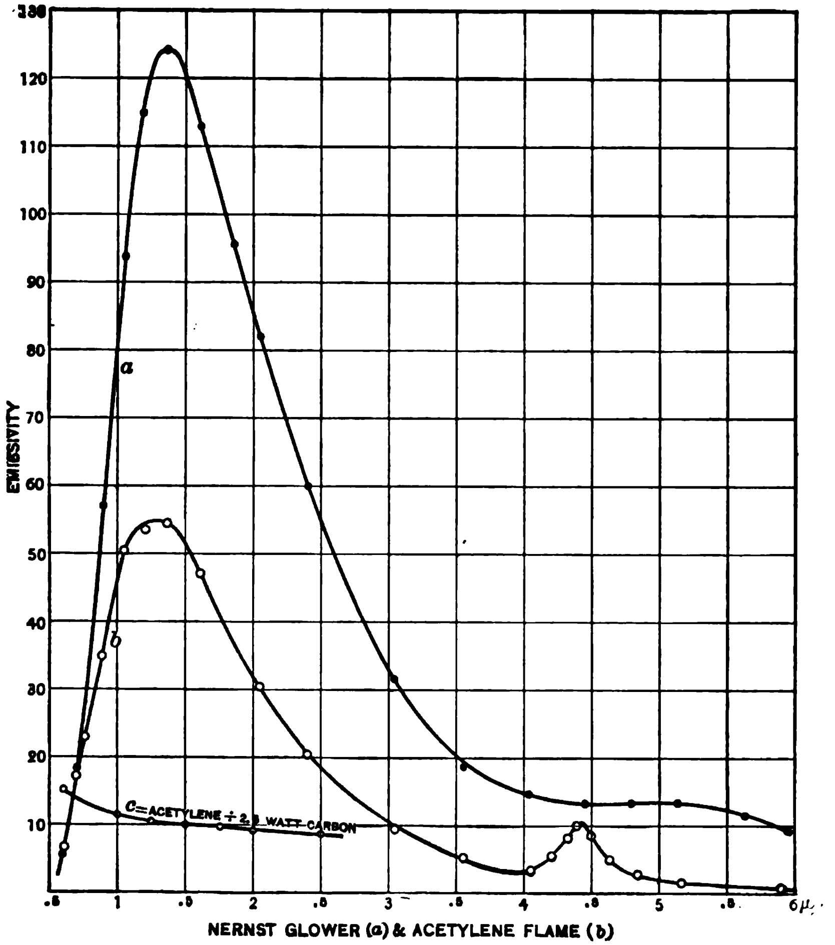

Fig. 7

flame. The radiation curves are entirely different in these two radiators and while the Nernst emitted the more "light," it was of a type not the most useful to the eye. The ratio of the areas of these two energy curves is (*a* : *b*) 84 : 34; the $\lambda_{max} = 1.35\mu$ and 1.25μ respectively.

5. ABSORPTIVITY OF AN ACETYLENE FLAME

The general notion seems to prevail that amorphous carbon in the form of "soot" or "lampblack" is a turbid medium, which has the property of an increase in transparency with increase in wave length. The few experiments now at hand on the absorptivity of a layer of soot at room temperatures indicate a high absorptivity in the visible spectrum which decreases uniformly but rapidly as we go into the infra-red. There are so many forms of amorphous carbon that this should hardly be considered a general rule without further investigation. Furthermore, the nature of the medium in which the particles are suspended must also be considered, whether the surrounding medium is a hot or a cold gas, or a liquid, as in the case of asphaltum varnish. In this respect, as will be noticed presently, the incandescent particles in the acetylene flame are not unlike colloidal suspensions of metals in which there is usually a distinct absorption band.

The present examination of the absorptivity of an acetylene flame was undertaken to verify the previous work by Ladenburg,[16] whose absorptivity curve (see Fig. 9) is smooth and continuous in the region of .7μ, where there should be an absorption band, if the acetylene flame has a true emission band in this part of the spectrum. The discovery of a fairly well defined absorption band in the visible spectrum came as a distinct surprise, for it was the expectation to find a uniform increase in absorption as we go into the ultra-violet, as is generally supposed to be the case, and as indicated in Ladenburg's curves, which, however, stop at .7μ. A subsequent search of the literature on the absorption by lampblack shows that, even in the cold state, there are some forms of carbon (or hydrocarbon ?) which exhibit an absorption band in the visible spectrum. In 1886, Nichols[17] published the results of an investigation of two specimens of lampblack, both of which showed a maximum of absorption in the region of .52μ, the transmitting power being considerably greater in the red and in the violet. Subsequently he published measurements upon the age coating in incandescent lamps, made by Messrs. Moore and Ling, in which it was shown [18] that the absorption of light by the deposit of carbon upon the glass bulb of a lamp with a treated carbon filament, was greatest in the region of .635μ. It is interesting to note that the age coating on the bulb of an incandescent lamp, containing an untreated carbon filament, did not show a maximum absorption in the visible spectrum, behaving in this respect like lampblack deposited from flames.[19]

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[16] Ladenburg, Phys. Zs., **7**, p. 697; 1906.

[17] Nichols, Trans. Kansas Academy of Science, **10**, p. 37, 1886; Phys. Rev., **13**, p. 378; 1901.

The structure of the carbon particles in the acetylene flame with their maximum absorption in the visible spectrum are therefore not very unlike some of the aforesaid "metallic" deposits from such vapors as gasoline or benzine on a treated carbon filament. By heating a strip of platinum in an inclosed vessel and then introducing acetylene, similar metallic films may be formed, which are easily removed and mounted on a glass plate.[19a]

The first indication of an increased transparency in the acetylene flame, in the violet, came from an examination of the ratios of its spectral emissivities with those of carbon filaments. These ratios show a decided maximum in the visible spectrum. This is illustrated in Fig. 8, in which curve *c* gives the ratios of emissivities of acetylene (from Fig. 4) divided by the emissivities of a graphitized carbon ("Gem") filament which was operated on 2.5 w. p. m. h. c. A similar curve, *c* Fig. 7, gives these ratios to 2.5μ. In this case the flat side of the flame radiated into the spectrometer slit. Curve *b* gives the ratios of emissivities of the acetylene flame to the emissivities of the graphitized carbon filament, when the flame radiated edgewise into the spectrobolometer. In these comparisons a glass prism was used with the quartz spectroradiometer. Using a quartz prism to obtain the two spectral energy curves, curve *d* gives the ratios of the emissivities of acetylene divided by the emissivities of a treated carbon lamp on 4 w. p. m. h. c. Curve *a* gives the ratios of acetylene to the emissivities of a Nernst glower, on normal operation. The depression observable at .48μ to .52μ in the preceding curves is also observable in this one; but since it is unknown whether the glower has a band of selective emission in this region the data is not so convincing.

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[18] Nichols, Amer. Jour. Sci., **34**, p. 277; 1892.

[19] Stark, Ann. der Phys., **62**, p. 351; 1897.

[19a] Since writing this paper, Dr. Nutting has kindly made a spectrophotometric examination of the age coating on the glass walls of commercial incandescent lamps containing "treated" filaments and graphitized carbon ("Gem") filaments. The lamps were prepared for me by Mr. Mulligan. The deposits were heavy, to avoid errors in observations. In neither case was a distinct absorption band found in the visible spectrum. The absorption decreased uniformly from 49 per cent in the violet (.447μ) to 47 per cent in the red (.7μ) for a sample coating from a "treated" carbon filament. The coating from the graphitized filament absorbed 29 per cent in the violet, which decreased uniformly to 28 per cent in the red. The observation were repeated, with greater thoroughness, on a sample of "treated" carbon deposit, which absorbed 57 per cent in the violet and 51 per cent in the yellow, the accuracy being 1 part in 200.

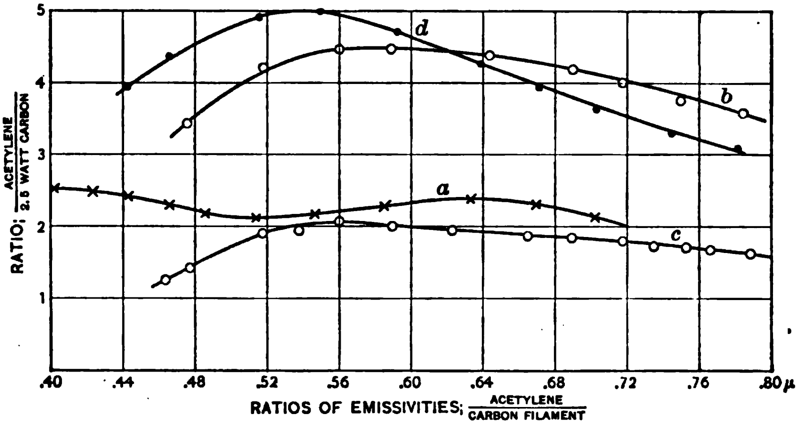

Fig. 8

In all these curves the region at .7μ to .72μ shows no sharp changes in curvature, such as would have to obtain in the presence of an emission band in this region. These spectroradiometric ratios are exactly analagous to the spectrophotometric data and since the original observations are accurate to at least 1 per cent (which accuracy can not be claimed with the spec rophotometer at .7μ) it is evident that the accuracy of the spectrophotometric data must be considered in doubt until further work has been done on that subject. In all these curves there is a pronounced maximum in the region of .56μ to .60μ, the variation in the position of the maximum being due to the difference in temperature of the carbon filament.

For curve *d* the black body temperature [20] of the treated carbon lamp on 4 w. p. m. h. c. is 1790° ± 20° C. This curve at $.7\mu$ is very similar to the one obtained with the spectrophotometer.[10] In the violet the spectrophotometric curves previously obtained,[10] and also those recently obtained by various observers in this Bureau, do not drop so rapidly as the aforesaid curves given in Fig. 8.

In the spectrophotometric comparisons of the acetylene flame against a black body at 1410° Abs. (a much lower temperature) Nichols and Merritt [21] found this maximum shifted over into the blue-green. However, the fact that the acetylene curve and the spectral energy curve of the black body at 1410° Abs. do not coincide is hardly evidence of selective emission, for the temperature of the acetylene flame is about 1800° C and hence would, under ordinary circumstances, emit the more light in the blue and violet part of the spectrum; but the important point is that their energy curve of acetylene shows a marked elevation in the blue-green.

While all this data can now, at the conclusion of the work, be cited as additional evidence of a transparent region in the violet of the acetylene flame, the first discovery of this transparency, by measuring the absorptivity directly, could not be supported by such convincing proof, and three distinct series of experiments were made, during an interval of four months, in order to be certain that the whole is not due to instrumental errors.

In the first series of measurements of the absorptivity of the acetylene flame an image of Nernst glower was projected upon the slit of the quartz lens spectroradiometer (with light flint glass prism) by means of a 15 cm focal length silvered mirror. The flat acetylene flame was placed, in a fixed position, about 3 cm in front of the slit. Two shutters were provided; the one for preventing any radiation from entering the spectroradiometer slit, the other for preventing radiation from the Nernst glower from falling upon the acetylene flame. Suitable shields were of course provided to prevent errors due to stray light. Repeated experiments showed that observations could be repeated exactly on relighting the flame. The Nernst glower was operated constantly on a storage battery, to keep it at a uniform temperature. The order of observation consisted in (1) setting the spectroradiometer circle to some definite wave length; (2) observing the galvanometer reading due to the acetylene flame; (3) observing the galvanometer reading when both the acetylene flame and the Nernst glower radiated into the slit; (4) with the acetylene flame extinguished, observing the radiation from the Nernst glower; and (5) usually repeating the complete series in the reverse order. From 10 to 15 observations were therefore obtained for each of the three steps, or from 30 to 45 at any spectrometer setting. The absorptivity is (2) + (4) − (3) ÷ (4). In this manner curve *a*, Fig. 9, was obtained. The cone of light from the glower covered the greater part of the thin central portion of the acetylene flame; but only a strip of the flame,

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[20] This Bulletin, **6**, p. 326; 1910.

[21] Nichols and Merritt, Phys. Rev., **30**, p. 328; 1910.

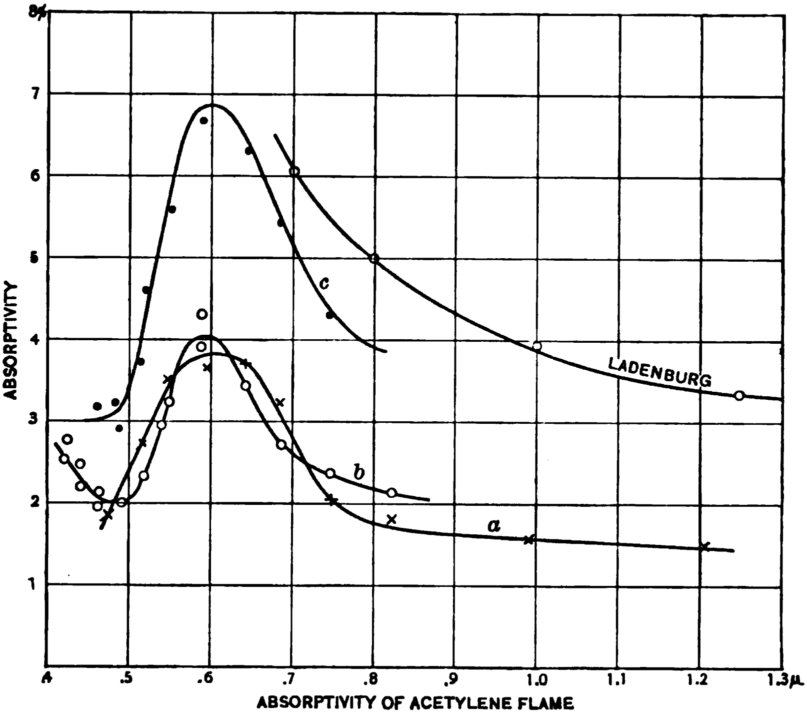

Fig. 9

about 5 mm wide, shone upon the prism face. The absorptivities are therefore only relative values. About four months later the work was taken up anew, to verify these observations, by using a thicker absorbing layer, but other instrumental details remaining as before. For this purpose two flat flames were placed as close together as was possible, and the absorption by the two flames was observed. The deflections for the two flames were, of course, much greater and permitted observations farther into the violet than in the previous experiment. The absorption band, curve *b*, Fig. 9, came out much sharper than with the thinner flame. Moreover, there appears to be an absorption minimum in the region of .48μ to .5μ. It is important to notice that the depression in the curves, at .5μ, is greatly magnified in Fig. 9, and hence, at a first glance, may appear deceptive. The total variation in the absorptivity is so small that it would be difficult to observe a change in emissivity in this part of the spectrum, because of the smallness of the galvanometer deflections, and the rapid change in the spectral energy curve as indicated in Fig. 4. The slight depression at .52 to .54μ observable in Fig. 4 is probably due to the increased transparency of the acetylene flame, but it is not much greater than experimental error.

There still being reasons for doubt in this matter the work was repeated, using Ladenburg's method in which an image of a thick (2 mm diameter) Nernst glower was projected normally upon the acetylene flame which stood flatwise back of a metal screen, with a slit 10 x 2 mm area. The radiation from the glower and the acetylene flame, passing through this slit was received upon a second mirror which projected an image of the two radiators (the slit) upon the spectrometer slit. The absorption in the second mirror reduced the intensity of the acetylene flame so much that observations were very difficult in the violet. The absorptivity curve *c* is practically the same as in the previous experiments. The absolute values of the absorptivities in the three experiments are not comparable, because different areas of the (flat surface of the) flame were examined. Ladenburg's curve is also given in this illustration as additional evidence of the absence of an absorption band at .7μ. In order to increase the absorptivity he placed the flame so that the flat side made an angle of 45° with the slit.

The sharp turn in the absorptivity curve at $.7\mu$ to $.8\mu$ must have a peculiar effect upon the emissivity curve, but it will not produce a true emission band. As a result of the absorption (emission) band at $.6\mu$, and of the rapid decrease in absorptivity at $.7\mu$, the spectral energy curve of the acetylene flame is much straighter (practically a straight line from $.64\mu$ to $.72\mu$) in this spectral region than obtains in metal and carbon filaments.

It will be an interesting investigation to determine whether the presence of an absorption band in the visible spectrum is a property of all flames containing incandescent carbon particles. In the low temperature flames, e. g. benzine, amyl acetate, etc., the difficulty will arise in obtaining sufficiently large deflections to make the test conclusive. A qualitative test may be obtained by simply taking the ratios of their emissivities against an untreated carbon filament. See Fig. 8. A special form of optical pyrometer would be the simplest instrument to use, provided it can be made sufficiently sensitive in the violet.

Heretofore it has generally been supposed that flame spectra [22] exhibit but two types of emission bands; (1) the sharp emission bands of the gases which are the heated combustion products of the gas used (e. g., the emission bands of CO_2 at 4.4μ, Fig. 6), and (2) the radiation from the incandescent carbon particles which, as in the case of the lamp filament, covers a wide portion of the infra-red spectrum with a maximum in region of 1.2μ to 1.5μ. But no really convincing data was at hand which indicated a true emission band in the visible spectrum. All the data herewith presented indicate such an emission band in the acetylene flame. The next question is the probable cause of this band. Some of the experiments on lampblack just quoted seem to indicate that the absorption is caused by the carbon particles (probably hydrocarbons) suspended in the heated gases. There seems to be a difference in the structure of the carbon (lampblack) deposited on a cold surface, which shows no absorption band in the visible,[19] and in the structure of carbon (hydrocarbon?) deposited on hot surfaces,

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[22] See The Illum. Eng., London, **8**, p. 261, etc., 1910, in which the various types of emission spectra are illustrated.

e. g., a deposit on the "treated carbon" filament of an incandescent lamp. The latter form when condensed on the walls of the lamp sometimes shows an absorption band in the visible spectrum.[18] The broadening or the sharpening of bands in various substances in solution, with change in temperature, does not seem to follow the same law. It is therefore possible that the broad region of absorption caused by the cold carbon particles is narrowed down into a sharp band when the particles are in a highly incandescent state.

The theoretical temperature of combustion of acetylene gas is of the order of 4000° to 5000° C at the moment of disruption of the acetylene molecule. Such a high temperature can not, of course, be maintained on account of the heat lost by conduction, convection, and radiation, so that the mean thermal temperature of the acetylene flame is about 1800° C. Similar emission bands in other substances have been ascribed to thermoluminescence and no doubt some will be willing to consider the selective emission in the visible spectrum of acetylene to be due to the emission of the acetylene molecule. By luminescence is meant an emissivity greater than that of a black body at the same temperature. An interesting case of a supposed thermoluminescence[23] is the peculiar diaphanous white light emitted by oligloclase when heated to a mean thermal temperature of 800° to 1000°. However, the incandescent carbon particles are at a temperature of at least 1800°, which fact, taken in connection with the experiments on the variation of emissivity with thickness and the comparison with the Nernst glower just described, seems sufficient evidence that the selective emission in the acetylene flame can be explained on a purely thermal basis, without invoking the hypothetical and unproven assumption of the presence of "luminescence."

6. SUMMARY

The present investigation of the acetylene flame had for its main object the exact determination of the emissivity and absorptivity in the visible part of the spectrum. This has required a special equipment of spectroradiometric apparatus and gas generators. The present results show that the earlier spectrophotometric data was misinterpreted; that the peculiar change in curvature in the spectrophotometric ratios at $.72\mu$ is not due to a true emission band but is due to a rapid increase in the transparency of the flame in the region of $.7\mu$ to $.8\mu$. The various curves herewith presented show no selective emission at $.7\mu$ in the sense of a true emission band or protuberance, rising sharply above the general trend of the spectral energy curve and merging into the latter at near-by regions—for example, at $.67\mu$ and $.73\mu$. The acetylene flame has a band of selective absorption (hence also of emission) extending throughout the visible spectrum with a maximum at about $.6\mu$. This absorption becomes more uniform beyond $.75\mu$, at which point there is a rather sharp turn in the absorptivity curve. This produces a much straighter spectral energy curve in the visible than obtains in carbon and metal filaments, and also results in a greater deficiency in the radiation in the infra-red. This is difficult to show in the spectral energy curve of acetylene, but is emphasized by taking ratios of emissivities by comparison with a radiator, which is more nearly like a black body. This procedure brings out small changes in curvature in a manner similar to the magnification of transformation points in cooling curves of a substance by using two thermocouples, the one of which is imbedded in a substance not having such transformation points. The method of taking ratios therefore commends itself in searching for a selective emission in the visible spectrum of low temperature flames.

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[23] Coblentz, Phys. Rev., 89, p. 561; 1909.

IV. SELECTIVE EMISSION OF THE WELSBACH MANTLE

1. HISTORICAL

It is beyond the scope of the present paper to give a complete account of the various experiments that have been made to explain the selective emission of the gas mantle perfected by Auer von Welsbach. A fairly complete account may be found in a recent paper by Fulweiler.[24]

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[24] The Theory of Flame and Incandescent Mantle Luminosity by Fulweiler. Trans. Illum. Eng. Soc., **4**, p. 65, 1909; The Illuminating Engineer (London), **2**; 1909.

That many of these experiments have been misdirected is evident; and it is equally true that the results obtained often seem to be seriously misquoted by subsequent writers. In view of the fact that even as late as the year 1895 the properties of the radiation from a uniformly heated enclosure were none too well understood, the experiments of St. John on the selective emission oxides [25] were novel. Two years prior to his work Violle [26] examined various oxides, heated to incandescence in a uniformly heated enclosure, and found that they all appeared at the same brightness, following Kirchoff's law. In the same manner Bunte [27] heated various oxides, including cerium and thorium, to 2000° in an electric furnace and found no special emissivity. In St. John's experiments the oxides were also heated in a furnace and after reaching a thermal equilibrium he observed their true emissive properties by introducing quickly, through the observing window, a cool porcelain tube at the end of which he could observe simultaneously his platinum comparison standard and the oxide. Since he received radiation only from the platinum and from the oxide and nothing from the enclosure, the black body effect was eliminated and he could observe their true emissive properties at known temperatures measured by the furnace.

In the experiments of Le Chatelier and Boudouard [28] they compared the brightness of different spectral regions of various oxides which they heated in a bunsen flame. To measure the temperatures they covered a thermojunction with the oxide under examination. They concluded that the Auer mantle emits no more than a black body, at the same temperature, and that the high emissivity in the visible is due to the coloring matter, cerium oxide, which is added to the thorium oxide.

Nernst and Bose [29] made a spectrophotometric comparison of the light from the Welsbach mantle with an incandescent lamp which was operated at different temperatures. They showed that the emissivity is low in the red, which imparts the greenish tint to the emitted light. In order to show that the flame gases have no influence on the light emission they formed the material, composing the Welsbach mantle, into a thin rod which they heated to the same temperature either in an oxyhydrogen flame or by means of an electric current. For thin threads of the material the ratios of the emissivities was practically constant throughout the visible spectrum. But for thick rods the ratios varied, which they explained by the fact that in the flame the rod is heated from without, while the electric current heats the rod from within. Unfortunately no spectrophotometric comparisons were made of the Auer mantle with the heated rod, which, as will be noticed in the work to be described presently, are decidedly different in their emissivities. Furthermore, no mention is made of the marked yellowish-green color which appears on warming the homogeneous rod of the mantle constituents.

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[25] St. John, Ann. der Phys. (8) **56**, p. 433; 1895.

[26] Violle, Compt. Rend., **117**, p. 33; 1893.

[27] Bunte, Bull. Soc. Franc, Paris, **114**, p. 2; 1898.

[28] Le Chatelier and Boudouard, Compt. Rend., **126**, p. 1861; 1898.

[29] Nernst and Bose, Phys. Zs., **1**, p. 289; 1900.

In the aforecited papers the general conclusion arrived at was that the high light emissivity of the Welsbach mantle is due to the finely divided particles of cerium oxide which are held in suspension, or perhaps in solid solution, in the thorium oxide. Since the cerium oxide has a high absorption for wave lengths shorter than the yellow, which would produce a high emissivity throughout this whole region, this is not an unreasonable conclusion. However, arguments have been presented to support the view that catalysis [30] in the gas flame causes a localized and more rapid combustion, and therefore causes a higher temperature than would be possible in the mantle of pure oxide. Here the catalytic action is supposed to be something similar to that of a jet of gas impinging upon a piece of hot platinum, which is then heated to a higher temperature by the unignited gas. In the mantle the most efficient mixture is about 99 per cent thorium oxide and 1 per cent of cerium oxide, and it is not clear why this particular ratio should be most efficient for the catalytic action. On the other hand, this optimum ratio makes the explanation tenable on the emissivity basis; for when the proportional part of ceria falls below the above amount the absorption, and hence the emission, would not be so complete in the region of the blue and the green, while if the per cent of ceria exceeds this optimum value the emissivity in the long waves becomes more prominent, as has been shown by experiment. Simply increasing the thickness of the radiating layer should have this same effect (if this is the true explanation of the observations), as shown in the experimental part of the present paper. If catalytic action has any marked effect, locally, in raising the temperature of the oxides then the mean temperature of the flame should be increased. This is contradicted by the experiments of White and Travers [31] who showed that the thoria-ceria mantle is at a lower temperature than a mantle of pure thoria, and that in general the mantles were about 130° C below the temperature of the flame.

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[30] Lewes, Chem. News, **91**, p. 62; 1905. Swinton, Proc. Roy. Soc. Lond. A, **65**, p. 115.

Previous experiments on the spectral energy distribution of the Welsbach mantle, of interest in the present work, were made by Rubens [32] who showed that in the region of 1μ to 5μ there is but little energy emitted, while in the green and yellow the spectral energy curve corresponds closely with that of a black body at 1800 Abs.

2. THE VISIBLE SPECTRUM

The strong selective emission in the visible spectrum of the Welsbach mantle is well known from previous spectrophotometric comparisons and from the recent spectroradiometric work of Rubens just quoted. The applicability of the mantle as a standard of radiation will require an extensive investigation of various mixtures of thorium and cerium. Even after specifying the relative proportions of the oxides used, the rate of gas consumption, etc., it does not appear, without further investigation, that conditions can be repeated with sufficient accuracy, so that it will probably be necessary to determine the spectral energy curve of a sample of each lot of mantles manufactured.

The peculiar energy distribution in the visible spectrum of the Welsbach mantle (of unknown composition) is illustrated in Fig. 10. The strong selective emission in the yellow-green, and the weakness of the radiation in the red ($.70\mu$) is very marked. The low emission in the red continues so throughout the infra-red. There is no marked maximum in the region of 1.2μ to 1.3μ as was supposed to be the case from the measurements made by Lummer and Pringsheim (Zs. für Beleuchtungswesen, vol. 10). It will be an interesting problem to determine the variation in the energy distribution in the visible spectrum with variation in the amount of cerium oxide used in the mantle.

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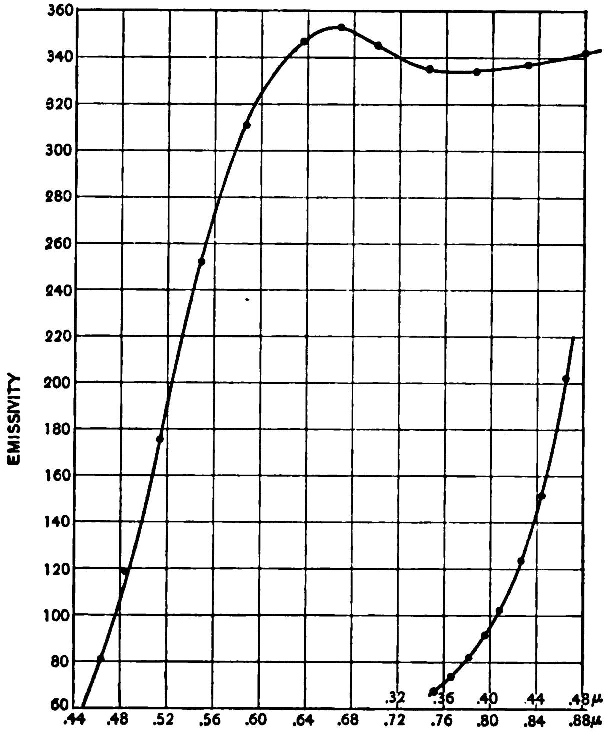
[31] White and Travers, Jour. Soc. Chem. Ind., **15**, p. 1012; 1902.

[32] Rubens, Ann. der Phys. (4) **18**, p. 725, 1905; **20**, p. 593; 1906.



SPECTRAL ENERGY CURVE
WELSBACH MANTLE

Fig. 10

3. COMPARISON OF GAS MANTLE WITH A SOLID GLOWER

The oxides are well adapted to the investigation of the variation in emissivity with the thickness of the radiating layer of the substance.

In a previous paper, the writer [33] gave the emission spectrum of a glower composed of 99 per cent thorium oxide and 1 per cent cerium oxide, which are closely the constituents of the Welsbach mantle. To verify these observations and to obtain quantitative data, the investigation was undertaken anew. The material used was obtained from new Welsbach mantles, which were ignited, to remove the organic matter, and the fine powdered oxides were squirted into glowers, which were then roasted in the same manner as is done with the commercial Nernst glower. This work was very kindly performed by the Westinghouse Nernst Lamp Company. Duplicate mantles were kept for the experiments on the spectral energy distribution of the mantle itself.

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[33] This Bulletin, 6, p. 318; 1909.

For the experiments on the gas mantle material (thoria ceria mixture) used as a glower, the solid rods were made into suitable lengths (12 mm long between the terminals and 0.77 mm diameter) and provided with platinum terminals. They were operated on the secondary of a transformer as in the previous work on the radiation from electrically heated oxides.

In order to have some rational basis for comparison, the glower was placed a short distance before the gas mantle (at a sufficient distance so that its conductivity was not affected by the mantle radiation) and the temperature of the glower was varied until it showed the same color as the hottest part of the mantle when viewed through monochromatic red, green, or blue glass. This calibration was done by two observers, and in three ways, to eliminate the effect of the structure of the mantle. In the first calibration (which consisted in noting the current and voltage in the primary of the transformer which was necessary to heat the glower to a certain temperature) the glower was brought in line with the vertical edge of the mantle, which avoided sighting on the open spaces in the mantle. In the second series, the observer stood at a great distance so that the eye could not distinguish the structure of the mantle. In the third calibration a metal screen was placed between the observer and the glower. The screen contained an opening of such a size as to cut off the view of the glower terminals. The three series of calibrations were in excellent agreement, as was also the various settings for intensity match by the two observers. The emissivity of the mantle in the red is so much less than that of the identical material when squirted into a solid homogeneous rod that an energy input of 22 watts sufficed to bring the glower to the same emissivity as the mantles in the red, while 24 watts were required to obtain the same emissivity as the mantle in the green. This low emissivity in the red of the Welsbach mantle is illustrated in Fig. 10. The maximum at .66μ varies with the composition of the mantle. The infra-red spectral energy curves were obtained with a fluorite prism and a vacuum bolometer. The problem consisted in observing the spectral energy curve of (the hottest part of) the Welsbach mantle heated by the usual gas burner. The mantle was then removed, the electrically heated glower was placed before the spectrometer slit and two series of spectral energy curves of the latter were obtained, the one series being for the same emissivity as the mantle in the red, and the second being for the same emissivity in the green.

The remarkable difference in the spectral energy distribution in the Welsbach gas mantle and the same material when operated as a solid glower is shown in Fig. 11. Curve *c* gives the spectral energy of the Welsbach gas mantle used without the glass chimney. The emission bands at 2.8μ and 4.4μ are due to the heated water vapor and CO_2 which are the products of combustion of a bunsen flame. The radiation from the mantle itself at 3μ corresponds somewhat with the dotted lines, curve *c*, which is essentially the same as previously observed by Rubens. Curve *a* gives the spectral energy distribution of the glower when operated on 24 watts (46 volts at terminals; .52 amp) which gave the same emissivity as the mantle in the green. Curve *b* shows the energy distribution of the same glower when operated on 22 watts (55 volts; .40 amp) which was the energy input required to give the same emissivity as the gas mantle, in the red.

The relative areas, as found with a planimeter, are: $a = 118$ units, $b = 55$, $c = 14$ ($c = 8.5$ units by omitting the emission bands). From this it appears that the solid glower emits about 8.5 times ($a \div c$) as much energy as the gas mantle in order to attain the same emissivity in the green. Of course, the glower emits the more "light." (The relative areas are: $a = .5$ and of $c = .2$ unit in the "visible spectrum.") But it is of a quality that is of little use in high efficiency illumination. To the eye such a glower appears a low red. It was therefore of interest to compare the mantle material in the form of the solid rod with a regular Nernst glower, which is composed of zirconium and yttrium oxides. The

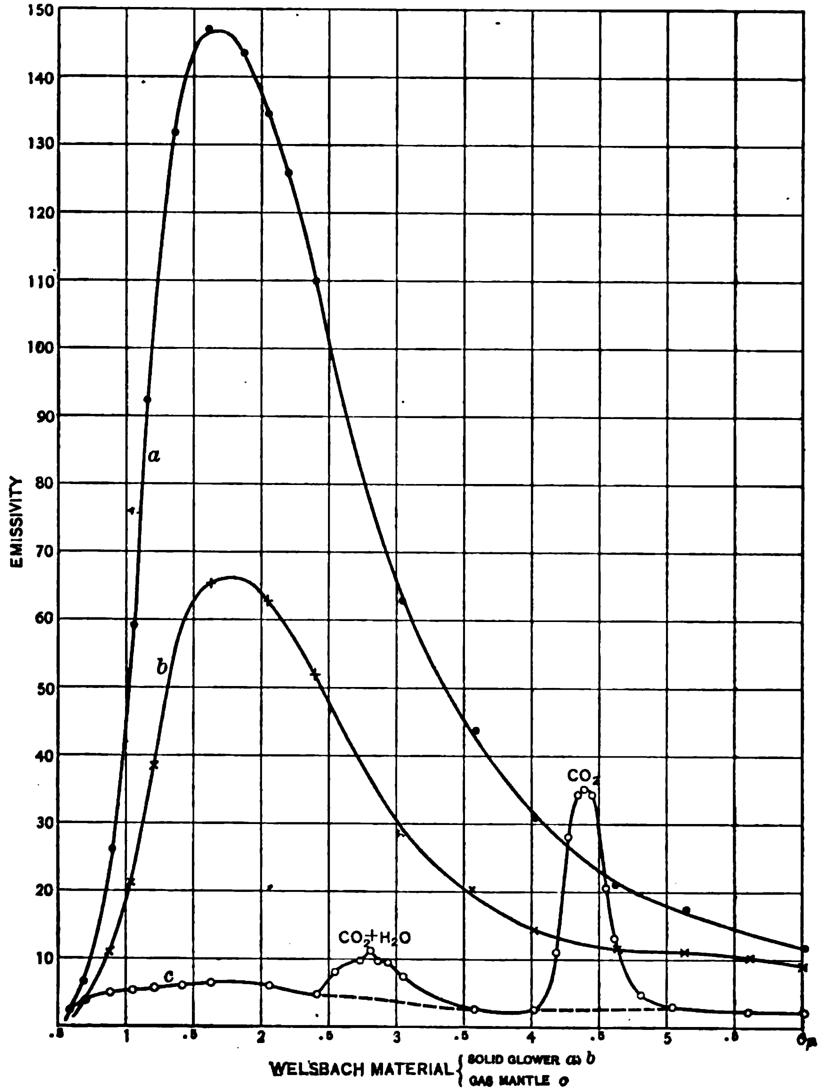
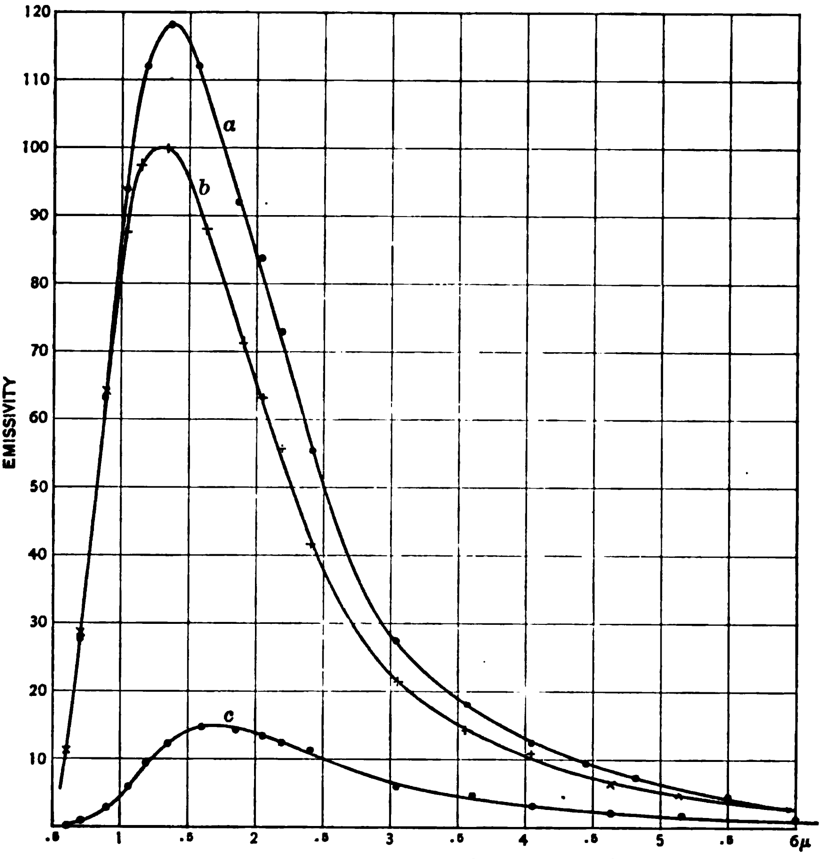


Fig. 11

Nernst glower used was the D. C. type, which was operated on 103 volts, 0.62 amp (64 watts) in order to obtain the same energy curve in the visible spectrum as a tungsten lamp operated on 1.2 w. p. m. h. c.—See Fig. 14. Viewed through either red, green, or blue glass, the regular Nernst glower and the rod of mantle material showed no marked difference in their emission. The rod of mantle material was therefore brought to the same emissivity



a WELSBACH MATERIAL (SOLID GLOWER)
b NERNST GLOWER

Fig. 12

as the Nernst glower, using red glass for the viewing screen. In making the equal emissivity setting the same results were obtained by viewing the two glowers placed side by side or so placed in the line of sight that they slightly overlapped.

The spectral energy curve of the Nernst glower, on practically normal operation (103 volts, D. C.; .62 amp) is shown in curve *b*, Fig. 12. The wave length of maximum emission lies at about $\lambda = 1.3\mu$. The spectral energy of the mantle material is shown in curve *a*. The energy input for the same emissivity as the Nernst glower was 56 watts (22 volts at terminals; 2.55 amp). Curve *c* is curve *a* of Fig. 11 drawn to the same scale. The maximum emission lies at 1.7μ. The realtive areas of these curves are: $a = 78$, $b = 64$, and $c = 12$ units. On a subsequent page it is shown that from the spectral energy curves of a Nernst glower and a tungsten lamp (the latter operated on 1.2 w. p. m. h. c.), set to the same emissivity in the visible spectrum, the Nernst glower is operating on about 2 w. p. m. h. c. No exact comparison can be made with the gas mantle because the quality of its light is so different in the red. The illustrations, however, show the great advantage which the mantle has over the thick glower of the same material. The latter must be heated to a much higher temperature to attain a luminous efficiency comparable with that of the gas mantle. It is to be noted, however, that in commercial operation the luminous efficiencies of the Welsbach mantle, the Nernst glower, and the tungsten filament are not markedly different, being of the order of 3 to 5 per cent of the total energy radiated. It may be noted that while the gas mantle has a higher luminous efficiency than a solid rod of the same material and also more efficient than a Nernst glower set to the same emissivity, the latter is the more efficienct of these two kinds of glowers.

The Welsbach mantle consists essentially of a woven framework of the purest cotton thread which has been boiled in potash to remove the silica. On ignition there is practically no ash. This cotton framework is impregnated with a solution of the nitrates of cerium and thorium and the cotton is removed by ignition. Thorium nitrate when heated expands into thin-walled tubes of considerable strength. This property, in addition to the removal of the numerous filaments composing the cotton threads, leaves the finished mantle of these oxides in an extremely porous state, which permits the particles to easily assume the temperature of the flame. Thorium oxide being white in color can emit but little in the visible spectrum. Cerium oxide is a rich yellow, absorbing all the violet, the blue, and into the green, and hence must emit the most energy in this region of the visible spectrum. If the thickness of the radiating layer of cerium oxide is small, then the effect of the selective emission is not noticeable in the spectral energy curve. If the thickness of the radiating layer is larger, the band of selective emission extends farther into the infra-red, and the flame temperature is lowered. In the mantle material, in the form of a solid rod, this excessive radiation is very apparent. For use in the bunsen flame, the Welsbach mantle of thoria and ceria in the ratio of about 99 to 1 seems to be the proper proportion for the most efficient illumination. When concentrated into a solid rod the low temperature of the flame and the rate of gas supplied is not sufficient to produce a satisfactory light, and, as noticed in the present illustrations, the temperature must be raised to that of the Nernst glower—2000° C—to produce an efficient illuminant. The specific emissivity is of course entirely different in the two cases, although their luminous efficiencies are not markedly different.

In conclusion it may be added that, while it is highly probable that the radiation from the Welsbach mantle is purely thermal, the problem being chiefly one of thickness of the radiating layer (concentration of the ceria particles), as illustrated in the present experiments, the question of the physical structure of the cerium oxide at high temperatures needs further consideration. In this connection, several observations may be recorded of the influence of temperature on the color of pigments.

It is a familiar fact that zinc oxide, which is perfectly white at room temperature, becomes a rich yellowish-green when heated above 400°. This change in its pigment color is due to a broadening of its absorption band from the ultra-violet into the visible spectrum. Cerium oxide has this same property to a very marked degree. This was first observed in the glower of the mantle material.

It was found that the solid rods of the Welsbach mantle material, used in the present experiments, emit (reflect) a yellowish green light when warmed to 400° to 500°, the color of the cold rod being white. The powdered mantle material does not show this effect to a marked extent. Thinking that this change in color might be due to some impurity in these particular rods, the glowers made directly from the pure thoria and ceria, described in a previous paper, were examined and found to exhibit this same property. Finally, the pure cerium oxide was examined. In spite of its rich yellow color, which made observation difficult, it turned to a decidedly yellowish-brown on warming. Other yellowish oxides, such as yttria, do not show this property (to a marked degree), which seems to belong to only certain substances. However, this is not a property of colored oxides, as shown by the behavior of zinc oxide, already cited, which at room temperatures is a pure white but which changes to a rich yellow or yellowish-green when heated above 400° to 500°. It is to be noted, however, that this is not a true light emission, such as obtains in the thermoluminescent fluorites (e. g., chlorophane) as may be easily shown by warming these oxides in a dark room, but is due to a change in the absorption of the incident white light and hence a change in the pigment color with change in temperature. This may account, in part, for the yellowish color often observable in street gas mantles when burning low in the daytime. In cerium oxide there seems to be merely a broadening of the absorption band, toward the red, with rise in temperature, and the interesting question is the magnitude of the effect of this temperature coefficient of absorption upon the emission of the gas mantle in the visible spectrum. If this change in absorption contributes (in emission) to more than the visible spectrum then some other yellow oxide, e. g., yttria, might be equally efficient. In this connection an investigation of the variation of the color of pigments with temperature might be useful.

The broadening of the absorption band in cerium oxide is similar to the previous observations on the broadening of the infra-red emission bands of the Nernst glower, with rise in temperature. Heretofore this change in emissivity, due to a broadening of the absorption band of cerium oxide (and hence a change in its pigment color), seems to have been overlooked. It seems evident that this broadening of the absorption (hence emission) band will contribute more to the emissivity in the visible spectrum than would a similarly colored substance in which the absorption band does not have such a large temperature coefficient. Hence the luminous efficiency of the Welsbach mantle is higher than it would be if the cerium oxide did not have the property of a change in pigment color, hence in its emissivity, with rise in temperature.

The facts just quoted, taken with the present experiments, seem to place the radiation of the Welsbach mantle on a purely thermal basis and renders it unnecessary to introduce the highly improbable hypothetical assumption of a catalytic action to account for the high light emissivity of the gas mantle. At the most, the effect of catalytic action is to raise the temperature of the gas, but it can hardly affect the spectral energy distribution. On the other hand, the thickness of the radiating layer (and perhaps the concentration of the cerium particles) has a very marked effect on the spectral energy distribution. In this connection it would be desirable to find the variation in emissivity of a given thickness of a solid rod in which the concentration of the cerium oxide is varied to compare with similar data on the mantle.

In connection with the foregoing experiments it is of course desirable to obtain quantitative data on the emissivity of some (pure) oxides with thickness. For this purpose samples of the same kind of glower material, squirted into rods varying from 0.2 mm to 3 mm in diameter have been prepared under standard conditions, and it is hoped that it will be possible to gain data on this question in the near future. These glowers also show a change in absorptivity (change in pigment color) on warming, but it is not so marked as in the glower of Welsbach mantle material. The pigment color is brownish, the color of the yttrium oxide, used in the glower, being a rich buff color, thus differing from the cerium oxide, which is a rich lemon tint. In previous communications attention was called to the fact that in metals the high light efficiency is due to a high emissivity (low reflectivity) in the visible spectrum, and a low emissivity (high reflectivity) in the ultra-red. In nonmetals the reflecting power is low, and the absorptivity is not dependent upon surface conditions of the substance. The emissivity is dependent mainly upon the absorptivity which in turn depends upon the thickness of the radiating layer. Ideal conditions would be fulfilled by a colored substance (e. g., cerium oxide) having a low absorption coefficient throughout the ultra-red, at low temperatures, but in which the absorption in the visible spectrum has a high temperature coefficient (as well as broadening of the absorption band, noticeable by a change in pigment color), so that at high temperatures the emissivity has increased enormously in the visible spectrum with only a moderate increase in the emissivity in the infra-red. This condition is partly fulfilled by the finely divided cerium oxide in the Welsbach mantle, but this condition is not fulfilled in the thick glower. This condition is partly fulfilled in thick layers of perfectly transparent substances, such as quartz, oligoclase, and aluminum oxide described in previous communications. In this case it was noticed that at low temperatures the spectral energy curves of these substances showed but little radiation at 1.5μ to 2μ; but at high temperatures the region in the visible spectrum to 1.5μ in the infra-red was suddenly filled up by a strong emission band. The aluminum oxide was the most remarkable of all, with an almost entire absence of radiation in the region of 3μ and with but a small emission in the region of 1.5μ where other substances, emitting a similar intense white light, have a strong emission band. Unfortunately the melting points of these substances are too low to make them useful illuminants.

V. MISCELLANEOUS SUBSTANCES

1. EMISSION OF ARC OF NERNST GLOWER MATERIALS

In the preceding experiments on the Welsbach mantle material used as a solid glower the rod broke, thus forming a high potential arc. Aside from a general increase in the spectral energy due to the radiation from the hot electrodes there seemed to be nothing unusual in the emissivity curve. The energy input remained practically unchanged.

In view of the fact that the radiation curve of the glower consists of emission bands which merge into a continuous spectrum, at high temperatures, it was of interest to determine whether these emission bands are observable in the vapors formed in the arc of these oxides. For this purpose an ordinary Nernst glower, which was broken through the center, was used. It was attached to the secondary (2000 volts) of a transformer and started by placing the two parts in contact and by heating them externally. After the glower became conducting, the two parts were separated, thus becoming an arc with electrodes of glower material. These electrodes were separated from 5 mm to 10 mm and an image of the arc vapor, which was a very faint white, was projected upon the spectrobolometer slit by means of a short-focus mirror.

The results obtained were entirely negative. Although the sensitivity of the vacuum bolometer was much higher than ordinarily used, neither selective emission bands nor regions of continuous radiation could be detected throughout the infra-red. The slightest trace of radiation from the hot electrodes was sufficient to produce large deflections even in the visible spectrum. The arc vapors were barely visible, and the absence of emission bands is probably to be ascribed to the thinness of the radiating layer.

2. COLOR MATCH VERSUS SPECTRAL INTENSITY MATCH

In a previous paper [34] experimental data was given indicating the spectral range in which there is at the same time a color match and a spectral intensity match. The importance of the work is evident from a consideration of the well-known fact that the eye is very sensitive to variations in color (comparisons in heterochromatic light, using an ordinary photometer) but is not so sensitive to variations in intensity (comparisons in monochromatic light, using a spectrophotometer). Hence, in comparing two widely different sources (e. g., carbon and tungsten), the estimation of a color match may be affected by the great difference in emissivities of the two sources in the deep red, and one can not be certain that their spectral energy curves coincide over a great length of the visible spectrum. It was found by Hyde [35] that on a color match the spectrophotometric curves of tungsten and carbon lamps coincide within the narrow spectral region of .5μ to .66μ. In this region it is an extremely easy matter to make spectrophotometric measurements. But if the attempt is made to extend the spectrophotometric comparisons toward the red, it is found that abruptly at .69μ to .70μ (at least for the writer's eyes) it is very difficult to make an accurate intensity match. Spectrophotometrically the region beyond .69μ can not be considered "well within the visible spectrum," because the eye is not sensitive enough for intensity comparisons in the deep red. But, as already stated, the eye is very sensitive to *differences in color*, and the light from .69μ to .75μ mixed with the blue and yellow may play an important part in the color match. The object, therefore, of the writer's experiment was to determine the magnitude of the departure in intensity match beyond .7μ when two lamps are set to a color match. In the previous work the spectrobolometric measurements at .69μ to .7μ were fraught with great difficulty, and the observed difference in intensity match, amounting to 1 to 2 per cent at .7μ, would have been given but little weight if it had not been for the more conclusive measurements at and beyond .75μ, where the intensity match was off by more than 5 per cent. This is well illustrated in Figs. 10 and 11 of the paper just quoted.[34]

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[34] This Bulletin, **6**, p. 301; 1910.

[35] Hyde, Elect. World, **55**, p. 1654; 1910.

The graph of ratios of emissivities, Fig. 11, is apparently a straight line, at .5μ to 2μ, inclined to the horizontal axis and intersecting it at an imperceptibly small angle in the visible spectrum; so small, indeed, that it can not be detected spectrophotometrically or radiometrically. If we do not admit this to be the case then we must assume that the ratio of emissivities is the same throughout the visible spectrum to .75μ, where the graph changes suddenly from a horizontal to an inclined position. This would necessitate the presence of a strong selective emission in the region of .7μ to .75μ (not unlike that which obtains in the visible spectrum of incandescent gold and copper), in order to keep the ratios the same as at .5μ to .66μ where no difference in intensity could be observed. Now the reflection curves of tungsten and carbon[36] show no indentations (such as occur in copper at .55μ) in the region of .75μ from which one can infer an extra emission in this region. The writer therefore concluded that the departure in intensity match already becomes perceptible at .7μ as observed. In one case[34] (see lower curve, Fig. 11) the intensity match seemed to continue out to .8μ, but since the color match was obtained without special care with an Ives colorimeter no great reliance was placed on the observations. Whether the graphs of ratios,

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[36] This Bulletin, 7, p. 55; 1911.

Fig. 11, are straight lines throughout the spectrum will probably depend upon the temperature (maximum emission with respect to the reflectivity curves) of the filaments. The comparison of these lamps for intensity match when on a color match was a piece of pioneering work which has opened up a field requiring further investigation. For the first time it gave us some idea, however crude, of the behavior of the eye in judging differences in color, and differences in intensity, of radiation lying in the extremes of the visible spectrum. But few seem to realize how limited the "visible spectrum" is in comparison with the total range of frequencies radiated by most solids. It is therefore possible to establish relations, e. g., color match, which immediately become inapplicable when we extend our observations beyond what we call the visible spectrum, especially beyond the region of $.5\mu$ to $.66\mu$.

The previous investigation arose from the writer's doubts as to the extent of the spectral region in which there is at the same time a *color match* and an *intensity match* of two substances, such as carbon and tungsten which (from a consideration of their reflectivities) must have very different spectral energy curves. The spectroradiometric apparatus described in the present paper is better adapted than that previously used to solve the color match problem and hence further data has been obtained.

It has always appeared to the writer that in a color match and in a spectral intensity match, of two sources having widely different spectral emissivities, the spectral energy curves really intersect at an extremely small angle so that, extending over a short spectral region, the two curves appear to be superposed, within the experimental errors of observation. The following experiments give further evidence to support this view.

The present experiments consisted in obtaining a spectral intensity match in the visible spectrum by means of a Lummer-Brodhum spectrophotometer, with a rotating sector (sector stationary and the beam of light is rotated) mentioned on a preceding page, and comparing this with a spectral energy match obtained radiometrically. The two sources selected were the Nernst glower and the tungsten lamp. The visible spectrum was examined with the quartz lens spectroradiometer, already described, while the infra-red was examined with a large mirror spectrometer and vacuum bolometer. The Nernst glower was the ordinary D. C. type, 13 mm long, 1 mm diameter, operated on 110 volts (at terminals), 0.67 amp. (74 watts), which is practically the normal operation. The tungsten lamp was the ordinary 110-volt type, which was operated on 1.2 w. p. m. h. c. The tungsten lamp, which

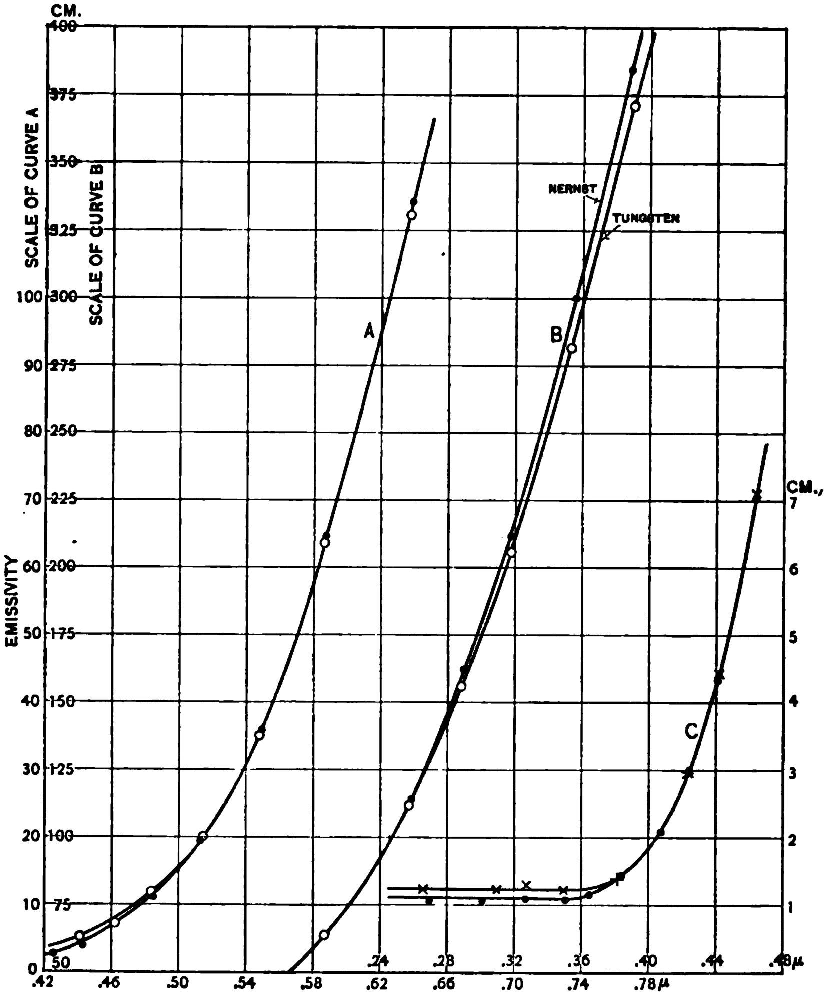

Fig. 13

had been carefully seasoned for a standard source of radiation, was made the standard in the spectrophotometric comparisons. The voltage of the Nernst glower was varied until the same photometric ratios were obtained throughout the visible spectrum to .69μ. This could be done with an apparent accuracy of 1 per cent. The spectral energy curves were then observed at the voltages required for a spectrophotometric match.

The prismatic energy curves for the visible spectrum are given in Fig. 13, the observations on the Nernst glower being represented by the dots (. . . . . .) and those on the tungsten filament by the circles (⊙⊙⊙⊙⊙⊙). The galvanometer deflections for the Nernst were 16 times as great as those from the tungsten lamp. When the two curves are superposed they coincide throughout the spectrum from .46μ to .66μ, where they begin to separate by a small amount, not greater than 1 per cent. At .68μ this lack of superposition amounts to 3 p. c.; at .74μ it amounts to 4 p. c.; and at .75μ it amounts to about 5 per cent. In the extreme violet the two curves also show a slight separation which probably would not be observable with the spectrophotometer. Exactly similar results were obtained with another glower. The main interest in the present experiment lies in the extreme regions of the "visible" spectrum. The results obtained verify the writer's previous conclusion that, in a color match or in a spectrophotometric match, there is no true superposition of the spectral energy curves, but that the two curves intersect at an extremely small angle, so that it is possible to have an apparent superposition within the narrow confines limited by the maximum sensibility of the eye.

Curve *c*, Fig. 13, gives the spectral energy distribution of the Nernst glower in the ultra-violet and of a second glower (xxxx) similarly calibrated against the tungsten lamp. The spectral energy curves of these two glowers coincide throughout the visible spectrum. If properly seasoned, the glowers promise to be useful reference standards if not put to hard usage. The interesting point about curve *C* is the horizontal part between .24μ and .34μ, which is a measure of the scattered light in the instrument. This scattered light is supposed to be uniform over the whole field. For wave lengths less than .2μ the deflections increased somewhat. Whether this was due to extraneous light or due to radiations of wave length greater than 50μ, caused by the anomalous dispersion in quartz which would refract the extremely long rays into this spectral region was not determined, the significance of the observation not being noticed at the time when the work was done.

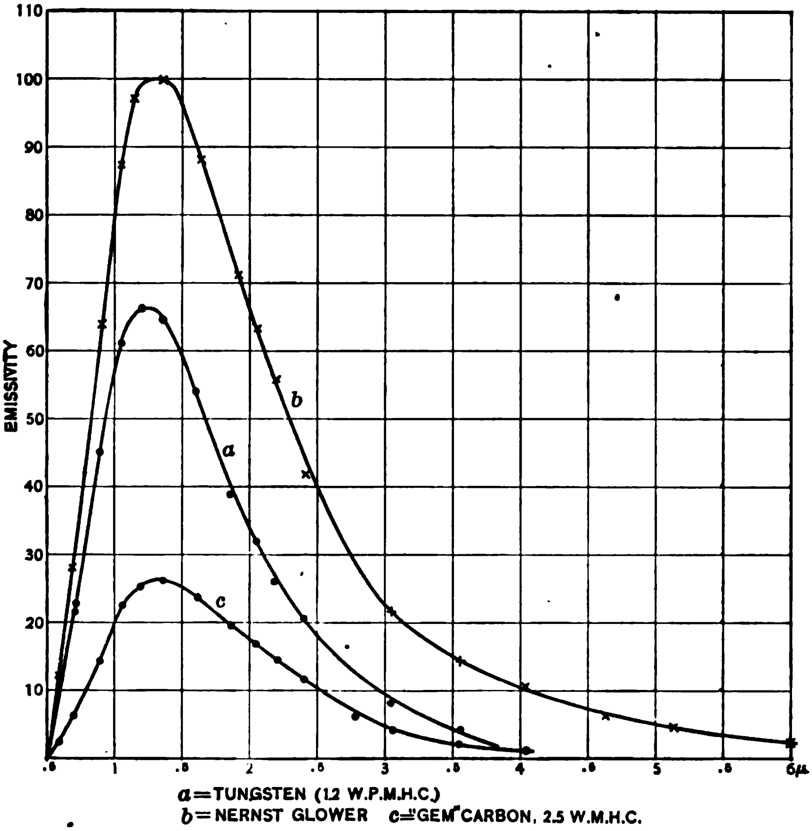

Fig. 14

The very marked difference in the emissivity of these two sources, already noticeable in Fig. 13, is illustrated in Fig. 14, in which curve *a* gives the spectral energy distribution of the tungsten lamp on 1.2 w. p. m. h. c. and curve *b* gives the spectral energy of the Nernst when it has the same energy distribution as the tungsten lamp in the visible spectrum—see Fig. 13. In the Nernst glower curve the $\lambda_{max} = 1.3\mu$ and in the tungsten curve the $\lambda_{max} = 1.22\mu$. The relative areas are: Nernst = 66, tungsten 37 units. This would make the glower about 2 w. p. c., but without proper reduction factors this can not be considered a fair rating. The interest in these curves lies in the illustration of the great difference (about 50 per cent) in the emissivities to produce the same spectral energy distribution in the visible spectrum.

The spectral energy curve of a "gem" (graphitized) carbon lamp on 2.5 w. p. m. h. c. is given in curve *c*, Fig. 14. The maximum emission is at $\lambda_{max} = 1.35\mu$, which is not very far removed from the Nernst glower.

WASHINGTON, November 8, 1910.

THE MEASUREMENT OF ELECTRICAL OSCILLATIONS IN THE RECEIVING ANTENNA

By L. W. Austin

In another article[1] it has been shown that the perikon detector can be standardized by comparing it with a thermo-element in a circuit to which it is coupled. If the thermo-element is calibrated so that the numerical value of the oscillating currents in the second circuit is known, then for the given conditions of frequency and coupling the perikon may be used for quantitative measurement of very small currents in the circuit to which it is coupled. This method has been developed for use in determining the numerical value of the currents in a wireless antenna when signals are being received.

The figure shows the connections used in this laboratory for this purpose. Here A E is the antenna circuit, with the inductances L_2 and L_3 for tuning and coupling. Below the inductance L_3 is a tellurium-constantan thermo-element[2] of 15 ohms resistance attached to a galvanometer G_2 of 8 ohms resistance giving 1 mm for $1.8 10^{-8}$ amp. Between the thermo-element and earth a variable air condenser C_2 of 0.001 mf capacity may be connected for tuning purposes when the received signals are of very short wave length. The detector circuit consists of an inductance L_4, a stopping condenser K of 0.04 mf capacity, and the perikon detector D, with its galvanometer G, of 2000 ohms resistance having a sensitiveness $1.28 10^{-9}$ amp per mm of scale deflection.

Before the measurements are begun the thermo-element must first be calibrated with high-frequency currents by comparison with a sensitive hot wire ammeter read by mirror and scale.[3] The resistance of the ammeter used in this experiment is 15 ohms, and at 1 meter scale distance 1 milliampere gives an appreciable deflection. With the circuits connected as shown in the figure, the antenna is tuned to the incoming signals, which for purposes of measurement should preferably be long dashes, and the coupling between L_3 and L_4 adjusted so that the galvanometer attached to the perikon gives a maximum deflection.[4] When the signals have ceased, the buzzer-exciter circuit $L_1 C_1$ is adjusted to resonance with the antenna circuit and coupled to it just closely enough so that a readable deflection is produced on the thermo-element galvanometer, while a large deflection is produced on the galvanometer attached to the perikon. The ratio of these deflections enables us at once to calculate the number of microamperes flowing in the antenna corresponding to any given deflection of the galvanometer, assuming that the deflections are proportional to the square of the current. The error in this assumption can be safely considered to be less than the errors of observation due to the fluctuations of the incoming signals themselves, provided the inductive reactance of the untuned circuit be kept less than the resistance of the detector.[5] Still greater accuracy may be obtained by adjusting the exciter circuit used in the comparison of the thermo-element and perikon to the same decrement as that of the

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[1] This Bulletin, **6**, p. 530; 1910.

[2] This Bulletin, **7**, p. 301; 1911.

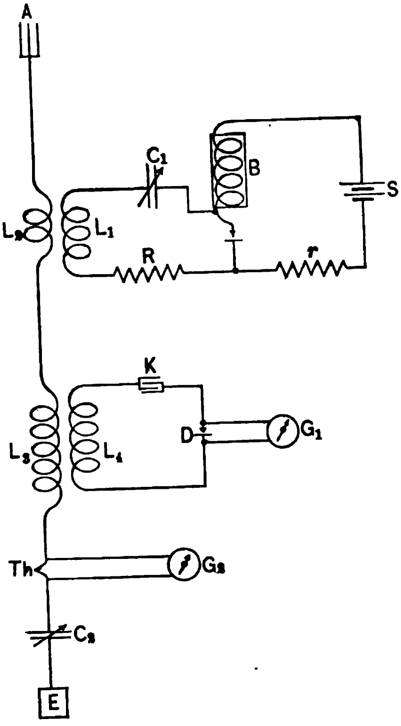

Fig. 1

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[3] Electrical World, **49**, p. 308, 1907.

[4] The coupling is made just loose enough so that the deflection begins to fall.

[5] Zenneck, Leitfaden der drahtlosen Telegraphie, p. 78.

sending station. This can easily be done by throwing the antenna out of tune while the signals are being received, so that the deflections of the perikon galvanometer are reduced to one-half. A fine-wire resistance R is then introduced into the exciter circuit until the same variation in the tuning of the antenna reduces the deflections due to the exciter to one-half. The exciter circuit then represents fully the sending station. This method also permits us to determine directly the numerical value of the decrement of the incoming waves. As a matter of fact, the errors in measurement of current due to differences between the damping of the exciter and of the sending station will be small if the decrement of the exciter be set anywhere from 0.15 to 0.3, since the variation in the ratio of the currents in the antenna and untuned detector circuits depends very little on the sending damping except when this is extremely small.

If the effective resistance of the receiving circuit as a whole be known, the amount of the received energy can be calculated, thus giving an opportunity for experimental determination of the ratio of radiated and received energy under different circumstances and at different distances.

The galvanometer used with the perikon is considerably more sensitive than any telephone, for long dashes it gives about 3 millimeters deflection for the weakest signals audible in the best telephones in the laboratory. This makes it possible to make measurements with fair accuracy on any signals which are detectable with the ordinary receiving apparatus.[6]

In regard to the accuracy of the method, of course it must be admitted that it depends on two exterpolation calibrations, but careful measurements indicate that the proportionality of the galvanometer deflection and square of the current both in the case of the thermo-element and the perikon is quite perfect enough for the present purpose.

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[6] **Measurements on faint signals can of course only be made when atmospheric disturbances are absent.**

In the following table are given the data of a number of measurements of signals received from various stations:[7]

Sending Station	Rated Power	Wave Lengths	Approximate Distance	Perikon Deflection	Ratio Perikon to Thermo-element	Received Current	Effective Receiving Resistance	Received Energy
	kw	m	miles	mm		10^{-6} amp	ohms	10^{-9} watts
Philadelphia (Navy Yard)	3	750	100	32	457	56.3	25	8
Brant Rock	60	3750	350	330	1280	108	80	93.5
U. S. S. Salem (at New York)	10	1000	185	100	540	91	38	31.5
U. S. S. Birmingham (at sea)	10	1000	300	115	540	98.3	38	36.5
Washington (Navy Yard)	2	900	6	Read directly on thermo-element.		1400	25	4900

1 mm on thermo-element galvanometer=213.10^{-6} amp A. C.

The table is self-explanatory. The higher land absorption is well shown in the cases of the Salem and the Birmingham. With the same power and approximately the same amount of energy radiated, the Birmingham delivered more energy at the receiving station at a distance of 300 miles than the Salem at 185, the path of the Salem's radiation being all the way overland, while the Birmingham's was for more than two-thirds of the way oversea.

The Birmingham's radiated energy may be calculated as follows: The height of the flat top antenna was approximately 40 meters and the wave length 1000 meters; from the Hertz radiation formula[8]

$$R = 1600\frac{h^2}{\lambda^2} = 2.57 \text{ ohms.}$$

The antenna current was 33 amperes.

The radiated enery

$$E = 33^2 \times 2.57 = 2.8 \ .10^3 \text{ watts.}$$

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[7] All the measurements were made during the daytime.

[8] See Rüdenburg, Ann. d. Phys., **25**, p. 446; 1908.

The ratio of received to radiated energy

$$\eta = \frac{36.5 \cdot 10^{-8}}{2.8 \cdot 10^{3}} = 1.30 \cdot 10^{-10}$$

For stronger signals the received energy may, of course, be measured directly on the thermoelement in the antenna, the perikon circuit being removed or coupled so loosely that no appreciable energy is taken up. By the last arrangement watch can be kept by means of a telephone attached to the perikon to see that no station or other disturbance comes in to affect the measurements.

By this method the following results were obtained from the station at the Washington Navy Yard, 6 miles away:

Received current at the Bureau of Standards $I = 1.4 \cdot 10^{-3}$ amp.

High frequency resistance of receiving antenna $R = 25$ ohms. The received energy $E = I^2R = 4.9 \cdot 10^{-5}$ watts.

The navy yard station, rated at 2 K W, has a wave length of 900 meters and its flat top antenna has a height of 55 meters. From the radiation formula, $R = 5.92$ ohms. The current in the antenna during the experiment was 13 amp. Hence the radiated energy

$$E = 1 \cdot 10^{3} \text{ watts.}$$

The ratio of energy received to that sent

$$\eta = \frac{4.9 \cdot 10^{-5}}{1 \cdot 10^{3}} = 4.9 \cdot 10^{-8}$$

This ratio, considering the short distance, is very small and is to be explained by the fact that the path of the waves lay practically all the way over the city of Washington.

U. S. NAVAL WIRELESS TELEGRAPHIC LABORATORY.
Washington, October 1, 1910.

SOME EXPERIMENTS WITH COUPLED HIGH FREQUENCY CIRCUITS

By L. W. Austin

1. INTRODUCTION

Very little experimental data has been given on the relative magnitudes of the currents in coupled circuits under different conditions of coupling. Fischer[1] has shown that, when a circuit containing a spark gap is coupled to a second oscillatory circuit and this second circuit in turn very loosely coupled to a third circuit containing a thermoelement, the current in the third circuit shows a well-marked maximum for a given degree of coupling between the first and second circuits, the current in the third circuit decreasing when the coupling between the first and second is either increased or decreased from this most favorable value. A very remarkable fact brought out in this paper is that for small degrees of damping the best results are to be obtained when the mutual inductance between the first and second circuits is extremely small. The reason for this behavior of high-frequency transformers with damped oscillations can be easily qualitatively explained by considering the reaction of the circuit receiving the energy on the circuit from which the energy is received. As the coupling between the two is increased the receiving circuit tends to draw a greater amount of energy out of the sending circuit, and hence acts as an increasing resistance introduced into the sending circuit, increasing its damping and decreasing the amplitude of the oscillations. It appears desirable that further quantitative data on this subject should be given and it is with this object that the present work has been taken up.

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[1] C. Fischer, Ann. d. Phys., vol. **22**, p. 265, 1907.

2. THE SOURCE OF THE OSCILLATIONS

For convenience in experimentation it was desired to set up the apparatus in a moderately small space, and this precluded the use of powerful spark apparatus on account of the direct action of the spark circuit on the detecting devices. Experiment showed that when feeble sparks carrying only a few milliamperes were employed undesirably large damping was introduced into the sending circuit. The buzzer method of exciting feebly damped oscillations by the whip-crack discharge,[2] it was found, did not give sufficient energy for the present purpose. Finally a satisfactory form of buzzer circuit[3] was determined on, which is shown in Fig. 1. In this B is a United States Signal Corps buzzer of the 1905 type excited by two storage cells with a regulating resistance and key in series. The oscillatory circuit which is connected around the break of the buzzer consisted of a variable air condenser C_1, having a maximum capacity of 0.005 microfarads and an inductance L_1 of 20 turns of No. 20 wire wound in a coil of approximately 10 cm diameter.[4] The value of this inductance was 0.062 millihenrys.

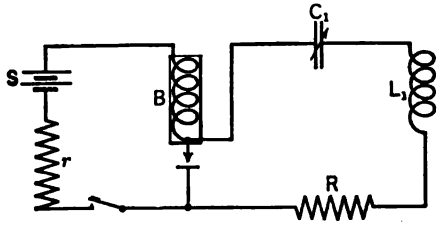

Fig. 1

This circuit, when the buzzer was properly adjusted, gave out very feebly damped oscillations, the logarithmic decrement, when no extra resistance was introduced, being between 1 and 2 percent.

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[2] M. Wien, Ann. d. Phys., **25**, p. 625, 1908, and L. W. Austin, this Bulletin, **6**, p. 149; 1908.

[3] L. W. Austin, this Bulletin, **6**, p. 528; 1910.

[4] It is to be understood that all the inductances employed in the work were wound in single layers.

With a proper adjustment of the buzzer, the direct effect of the spark on the thermoelements or other detectors used in the current measurements can be made negligible; sometimes, when the adjustment is most perfect, amounting to less than 0.0001 of the total deflection.

A second form of buzzer[5] circuit which, while it gives less energetic oscillations and involves the use of stronger coupling between the circuits, at the same time is easier of adjustment, especially for very long wave lengths, is shown in Fig. 2.

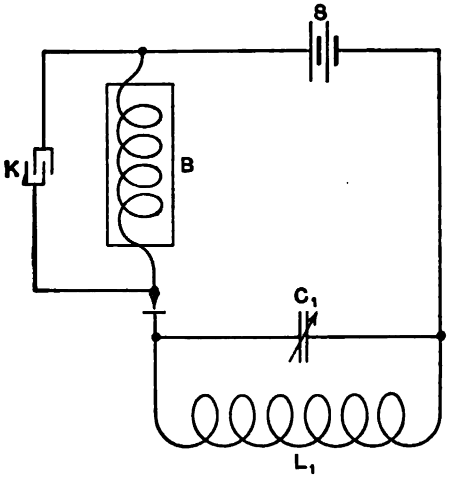

Fig. 2

Here B is the buzzer driven by one or more storage or dry cells with a regulating resistance in series. L_1 is an inductance, C_1 a variable tuning condenser, K a fixed condenser large enough to prevent sparks at the buzzer contact, which would produce a disturbance in the receiving apparatus. When the current is broken, the inertia of the current in L_1 charges the condenser C_1 and feebly damped oscillations are produced in the circuit L_1C_1. The damping may be increased by introducing resistance in this circuit.

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[5] Zenneck, Leitfaden der drahtlosen Telegraphie, p. 3.

3. THE THERMOELEMENTS

For a considerable portion of the current measurements thermoelements were required. These were constructed as follows: Two copper wires were placed side by side about 3 mm apart and embedded in insulating material with their ends protruding (Fig. 3). To the end of one of these was soldered about 5 mm of 0.02 mm platinum or constantan wire. To the other was soldered a short bit of No. 20 platinum wire, to the end of which a bead of tellurium had previously been attached when the platinum was white hot.[6] The end of the fine wire was next allowed to rest against the tellurium and the two were welded together electrically by means of a small induction coil with a high resistance in series with the secondary. The contact will be less fragile if the welding is done in an oxygen-free atmosphere. The resistance of a thermoelement prepared in this way may be anywhere from 5 to

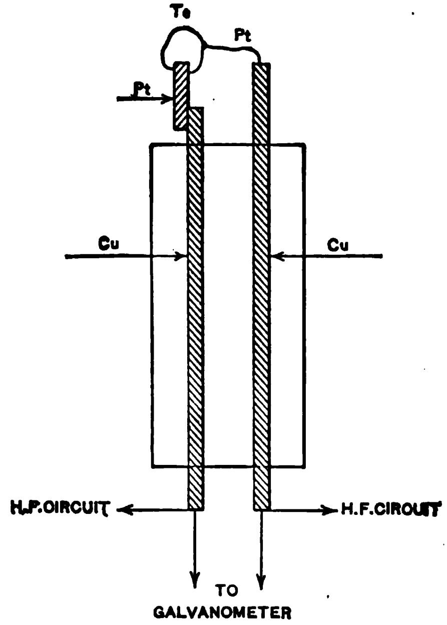

Fig. 3

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[6] White-hot platinum wire when inserted in tellurium forms practically a resistance-free contact.

50 ohms, according to the conditions of welding and the resistance of the fine wire, the lower resistance being somewhat more difficult to obtain. The thermoelement is next inclosed in a test tube, and, if likely to be handled roughly, the whole may be inclosed in a larger test tube with cotton or felt between the two.

TABLE I

Platinum-Constantan and Tellurium-Platinum Thermoelements in Series

Galvanometer Deflections		Ratio
Platinum-constantan	Tellurium-platinum	
2.2	62	28
4.0	108	27
6.2	176	28.5
9.1	255	28
18.5	510	27.5
20.3	560	27.5
24.6	700	28.5
29.1	810	28

Thermoelements prepared in this way, if carefully handled, are extremely stable and perfectly constant in their electrical properties over long periods. One thermoelement of 11 ohms resistance has now been in constant use in the laboratory for nearly two years and has shown no appreciable variation during the whole time. These thermoelements, on account of the nature of their construction, can not be calibrated by means of direct currents, but may be compared at least over the range of the larger high-frequency currents with a sensitive hot-wire meter which has already been calibrated, arranged for mirror and scale reading.[7] Comparison can, of course, be made also with wire thermoelements of ordinary types. Table I shows the admirable proportionality between the galvanometer deflections of a constantan platinum thermoelement already calibrated and those of the tellurium-platinum element.

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[7] The hot-wire instrument used was a General Electric Company's voltmeter employing a wire of 15 ohms resistance and giving full scale deflection for 240 milliamperes. By means of a mirror attached to the pointer or, less preferably, if the pointer itself be observed by a microscope, a current of 1 milliampere is readily readable. The constancy is all that could be desired. See Electrical World, Vol. XLIX, 1907, p. 308.

The 32-ohm thermoelement with the most sensitive galvanometer gave a deflection of about 1 mm for 120 microamperes.

4. THE CONTACT RECTIFIER

For measuring still smaller oscillatory currents, a contact rectifier was used, in which the contact was formed between a crystal of zinkite and one of chalco-pyrite. This combination goes under the trade name of the perikon detector. In its properties it resembles very closely the silicon-steel rectifier described in a former article[8] but is more easily adjusted and is somewhat more constant in its action. When used with a galvanometer as shown in Fig. 6 the galvanometer deflection is proportional to the square of the high frequency oscillations passing through the rectifier.[9]

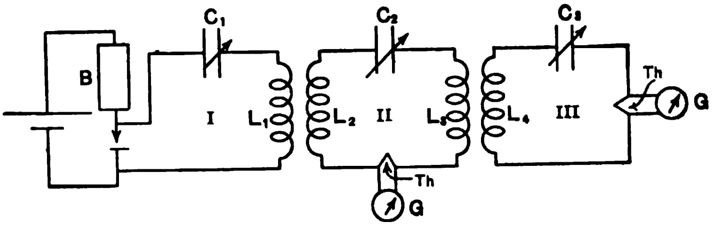

Fig. 4

5. METHOD OF OBSERVATION

The general scheme of the circuits is shown in Figs. 4 and 6. Here circuit I is the buzzer exciter circuit, already shown in detail in Fig. 1, circuit II a closed oscillatory circuit consisting of a coupling inductance L_2 of 0.03 millihenry, an inductance L_3 of 0.425 millihenry, and a variable air condenser C_2 having a maximum capacity of 0.001 microfarad. The circuit contains also a thermoelement Th of the type already described, across the terminals of which a galvanometer is connected. In Fig. 4, circuit III is a tuned circuit consisting of an inductance L_4 of 0.42 millihenry, a variable air condenser C_3 of 0.001 microfarad, and a thermoelement.

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[8] This Bulletin, 5, p. 133, 1908.

[9] This Bulletin, 6, p. 530; 1910.

In Fig. 6, circuit III is an untuned circuit consisting of an inductance L_4 of 0.42 millihenry, a fixed stopping condenser K of about 0.04 microfarad and a perikon detector D which can be connected to the galvanometer. On account of the high resistance of the perikon detector and the large capacity of the condenser, circuit III may be considered as strictly aperiodic.

The wave length used in all the experiments was 900 m and the sending decrement δ_1 was varied between 0.02 and 0.8 by inserting resistance in the oscillatory portion of the buzzer exciter circuit. The decrement of the exciter circuit was determined from the resonance curve, observed in a standard wave meter of known damping, when loosely coupled to the exciter, using the well known formula

$$\delta_1+\delta_2=\pi\frac{C_m-C}{C_m}\sqrt{\frac{I^2}{I^2_m-I^2}}$$

which expression becomes simplified to

$$\delta_1+\delta_2=\pi\frac{C_m-C}{C_m}$$

when the capacity change is just sufficient to make $I^2_m=2I^2$. Here C_m and I_m represent the values of the capacity and oscillatory current for resonance. The decrements in circuits II and III were determined similarly by exciting them with circuit I, after its decrement had been determined.

6. THE RELATION BETWEEN THE COUPLING AND THE CURRENT DISTRIBUTION IN TWO TUNED RECEIVING CIRCUITS

This case is represented by the circuits of Fig. 4. Here circuit I, very loosely coupled to circuit II, may be taken to represent a sending station adjusted to send out waves of but a single wave length. Circuit II with its 11-ohm thermoelement represents a receiving antenna of moderate dimensions, while circuit III, containing a thermoelement of 32 ohms, represents a tuned, closed receiving circuit coupled to the antenna.

TABLE II

Coupling and Currents in Circuits II and III

$\lambda=900$ m. $\delta_{II}=0.059$. $\delta_{III}=0.0996$. [I in milliamperes]

K	$\delta_1=0.02$		$\delta_1=0.16$		$\delta_1=0.8$	
	I^2_{II}	I^2_{III}	I^2_{II}	I^2_{III}	I^2_{II}	I^2_{III}
	(milliamperes)²		(milliamperes)²		(milliamperes)²	
0	16.9	....	16.9	....	16.9	....
0.010	.....	....	.....	....	....	....
.014	16.6	0.49	16.5	0.41	16.2	0.39
.020	15	1.08	15.3	.93	14.9	.86
.028	11.6	1.22	13.7	1.95	13.8	1.78
.030	10.7	2.60	12.5	2.56	....	....
.033	.....	....	.....	....	12.4	3.25
.037	7.05	3.67	8.95	4.02	11.0	4.13
.041	4.92	3.81	7.8	4.45	9.4	4.75
.049	2.01	3.56	5.45	4.80	8.4	5.60
.061	1.30	2.71	4.34	4.57	7.5	5.95
.073	.77	1.88	3.34	3.92	6.2	5.95
.099	.....	....	.....	....	5.5	5.75
.126	.....	....	.....	....	4.5	5.3

Table II and Fig. 5 give the results of a series of observations on three different values of sending decrement for various degrees of coupling *k* between circuits II and III. It is seen that as the coupling is increased the current in circuit II falls rapidly, while that in circuit III increases rapidly up to a given point. In this neighborhood both curves change their direction and both fall together as the coupling is further increased. From these curves it is seen that the current in circuit II falls more abruptly and at a smaller coupling the less the damping of the received wave trains. Similarly, the current in circuit III rises more rapidly and abruptly and with smaller coupling, in the case of the feebly damped trains. It is noticeable also that the maximum in the current of circuit III is much more marked with the feebly damped trains. In the case of a sending decrement $\delta_1=0.8$, the maximum is scarcely to be observed, the magnitude of the current remaining almost unchanged as the coupling is increased in strength beyond the

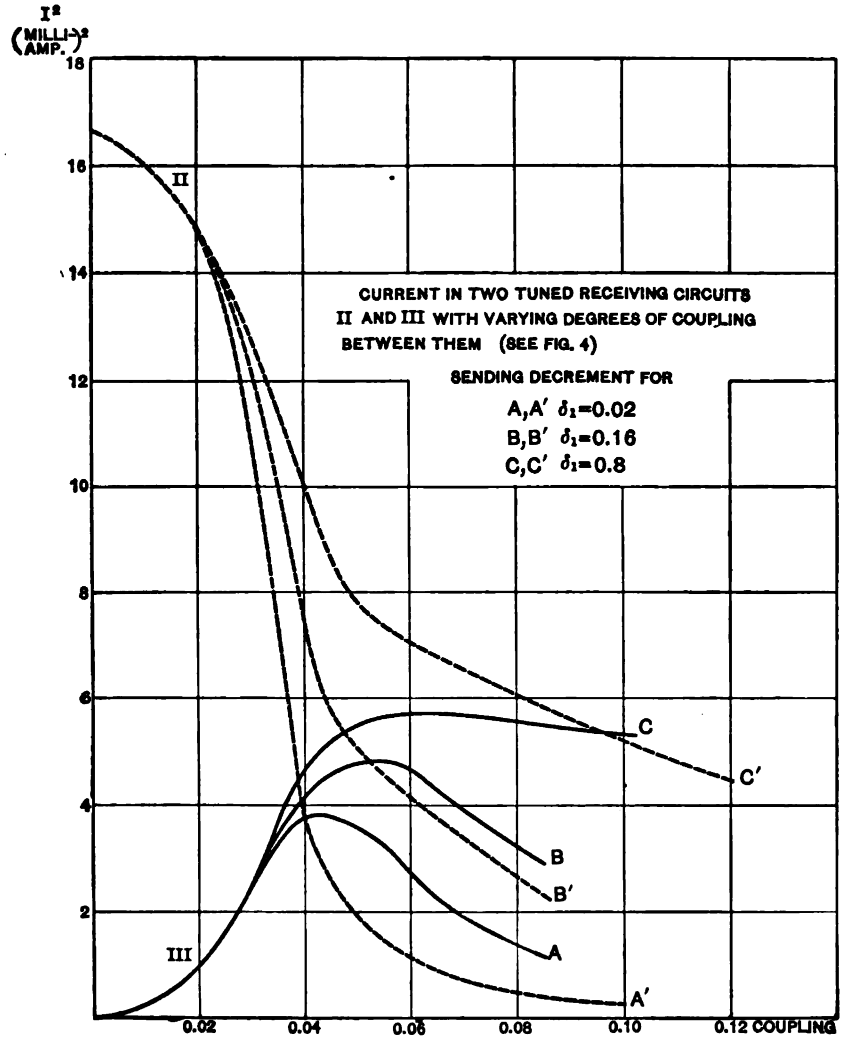

Fig. 5

point at which it has ceased to rise. It is also to be noted that the maximum amount of energy capable of being drawn into circuit III is relatively larger, the greater the sending decrement.

7. COUPLING AND CURRENT DISTRIBUTION BETWEEN A TUNED AND AN UNTUNED RECEIVING CIRCUIT

In several forms of wireless receiving apparatus the detector is contained in an untuned circuit coupled to the antenna. Such a case is represented in Fig. 6. Here, as before, circuit I represents the sending station, circuit II the antenna, which in this case contains a 32-ohm thermoelement, and circuit III, with its perikon detector and fixed condenser K, the untuned detector circuit.

It has been shown in another place that the deflections of a galvanometer attached to a perikon detector are proportional to the square of the current in a circuit to which it is coupled, for any given frequency.[10] It is strictly true, however, only when the resistance in the circuit is either larger or very much smaller than the inductive reactance of the circuit.[11]

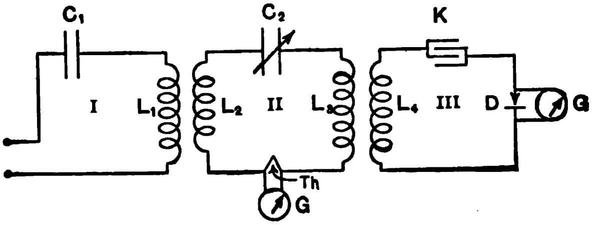

Fig. 6

Table III and Fig. 7 show the relations between the currents in circuits II and III for different degrees of coupling for a sending decrement 0.16. It is seen that the current in circuit III rises rapidly up to a certain degree of coupling, beyond which it falls slightly as the coupling is increased. Comparing Figs. 5 and 7, it appears that the position of the maximum current in circuit III occurs as would be expected, with a much stronger coupling when circuit III is untuned, and that the maximum itself is much less strongly marked. The curves are given for but one value of sending decrement, as it was found that the change in the form of the curve was but very slight, as the sending decrement was varied.

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[10] This Bulletin, 6, p. 530; 1910.

[11] Zenneck, Leitfaden der drahtlosen Telegraphie, p. 78.

TABLE III

Coupling and Currents, Circuit III Untuned

λ=900 m. δ_I=0.16 δ_{II}=0.13

K	Thermoelement Circuit II I^2_{II}	Perikon Circuit III Deflections
0	1.66	...
0.032	1.62	24
.057	1.51	131
.088	1.44	295
.115	1.38	423
.145	1.21	580
.212	.75	640
.463	.41	520
.570	.23	430
.655	.12	350

8. THE RELATION BETWEEN COUPLING AND SHARPNESS OF RESONANCE

It has already been stated that we may consider the coupling of a circuit containing resistance to another circuit as introducing a certain proportion of its resistance into the latter. This will not only decrease the amplitude of the oscillations in the circuit but will also increase its natural logarithmic decrement and decrease the sharpness of the resonance curve when it is brought into resonance with any circuit from which waves are being sent.

In order to observe this relationship quantitatively the detector circuit III shown in Fig. 6, containing a perikon detector of 2000 ohms resistance[12] connected to a galvanometer, was coupled inductively to circuit II with the thermoelement removed. This latter circuit was excited by the buzzer exciter. Under the conditions used, it was determined experimentally that the natural decrement of the buzzer exciter circuit was approximately 0.02 and that that of circuit II was very nearly the same. The damping of the system was then observed as the coupling between the circuits II and III was increased. The results are given in Table IV and Fig. 8. It is to be seen that the influence of the coupled detector on the damping is practically negligible for K=0.057

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[12] The resistance of rectifiers of this type is a variable quantity depending on the magnitude of the oscillatory current. See this Bulletin, **5**, p. 133; 1908.

and nearly so for K = 0.085, and that the values become very large as the coupling is increased to a maximum. If the buzzer exciter has a decrement of 0.12, corresponding to a rather feebly damped wireless sending station, and circuit II has a decrement of 0.13 representing a receiving antenna, Table IV shows that the damping due to the coupled detector remains relatively negligible until the coupling has been increased beyond 10 per cent.. The form of the curve in Fig. 8 indicates that the coupling damping increases with the mutual inductance until the point is reached where the current curve ceases to rise. (See Fig. 5.) The rise of the damping curve is then for a short distance very slight but with still closer coupling again rises abruptly.

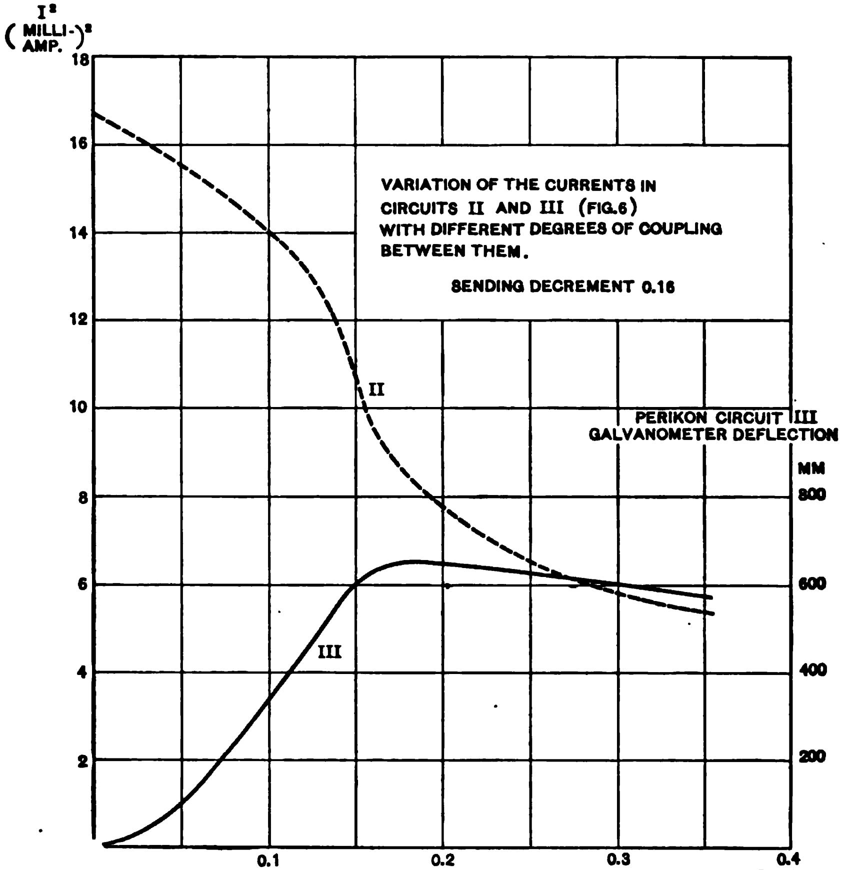

Fig. 7

TABLE IV

Coupling and Total Apparent Decrement

$\lambda = 900$ m

K	$\delta_I = 0.02$	$\delta_{II} = 0.02$	$\delta_I = 0.02$	$\delta_{II} = 0.13$	$\delta_I = 0.12$	$\delta_{II} = 0.13$
	Perikon deflections	$\Sigma\delta$	Perikon deflections	$\Sigma\delta$	Perikon deflections	$\Sigma\delta$
0.032	14	0.040	..	....	....	....
.039	54	.042	7	0.149	7.5	0.244
.057	200	.050	28	.151	27.5	.270
.085	410	.060	83	.162	66	.320
.114	450	.072	135	.179	92	.342
.148	430	.111	195	.196	130	.370
.212	340	.150	250	.239	156	.430
.303	280	.180	240	.294	154	.510
.463	230	.250	230	.380	150	.620
.570	185	.372	210	.510	132	.830
.655	115	.705	150	.840	100	1.110

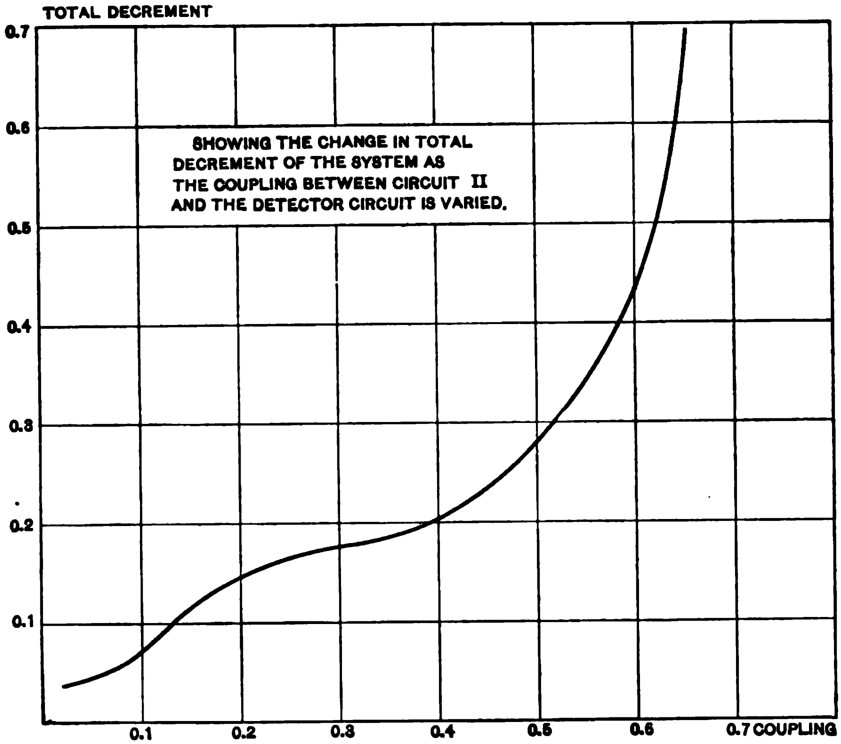

Fig. 8

9. DISCUSSION OF RESULTS

If the tables and curves be examined in regard to the quantitative relationship between the energy in the two circuits under special consideration in each case, it will be found that in the case of the more feebly damped oscillations the maximum of the I_{III}^2 curve in circuit III occurs at that degree of coupling for which the I_{II}^2 curve in circuit II has fallen to approximately one-fourth of its maximum value, while with increasing sending damping, the maximum for I_{III}^2 approaches the point at which I_{II}^2 falls to one-half.

The results obtained have also a practical bearing on the construction and method of use of receiving circuits. They show that for the greatest efficiency in working, the apparatus must be so arranged that the amount of energy withdrawn from the antenna may be varied until the point of maximum effect is obtained. If the detector is connected in shunt across an inductance the number of turns contained between the detector terminals should be variable and independent of the number of turns of the inductance which are used for tuning purposes. If the detector is connected around a condenser, it must have in series with it a small variable condenser which can be used to regulate the amount of energy flowing into the detector. By far the simplest and best method, however, is the inductive coupling of the untuned detector circuit to the antenna or to an intermediate tuned circuit, the coupling coils being arranged so as to be easily moved toward or away from each other by means of a rack and pinion or some similar device.

The portion of the work on the relation between coupling and sharpness of resonance also shows the importance of having means of varying the amount of energy drawn from the antenna circuit. The results show that if the coupling be made stronger than is required for the maximum effect in the detector, the damping is largely increased, resulting in an enormous loss in sharpness of tuning, while at a point a little before the maximum is reached the detector produces a comparatively feeble influence on the receiving damping and at the same time the intensity of the current in the detector is but little below its maximum value.

U. S. NAVAL WIRELESS TELEGRAPHIC LABORATORY,
Washington, D. C., May 1, 1910.

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SOME QUANTITATIVE EXPERIMENTS IN LONG-DISTANCE RADIOTELEGRAPHY

By L. W. Austin

During December, 1909, and the spring and summer of 1910 the Navy Department carried on long-distance wireless tests between the scout cruisers *Birmingham* and *Salem* and the large Fessenden station at Brant Rock, which was leased by the Government for this purpose. These tests were primarily for the determination of the range of communication between the two cruisers and between the cruisers and the Brant Rock station. The United States Naval Wireless Laboratory had charge of the taking of certain quantitative measurements in connection with these tests, and this enabled us to obtain scientific data in regard to the laws which govern the radiation and reception of electrical waves, and, what was of especial interest, to study the course of the so-called atmospheric absorption up to a distance of about one thousand miles. The following paper contains the results of this work.

It was shown by Duddell and Taylor[1] in experiments carried on between a land station and the steamer *Monarch* in the Irish Sea that the received current over water fell off very nearly in proportion to the distance. This law has since been verified by Tissot.[2]

As the data obtained during the July experiments were by far the most full and accurate, all the theoretical deductions have been based on these results and the others have been employed only for comparison and verification. The Brant Rock station, situated directly on the shore 20 miles south of Boston, employs for its antenna a steel tower 420 feet high and 3 feet in diameter thoroughly insulated at its base. From the top of the tower extend four arms 50 feet in length and from each of these two 300-foot cylindrical cages are drawn out by means of guys at an angle of about 45°. This forms a system of eight conductors spaced symmetrically about the tower. These cages are approximately 4 feet in diameter and consist of four wires each, separated by a system of hoops. The cages are insulated at the bottom and electrically connected to the steel tower at its top, thus forming a type of umbrella antenna. The inductance of the complete antenna system amounts to 0.055 millihenry, and the capacity is 0.0073 microfarad. The closed circuit was inductively coupled to the antenna just loosely enough so that but one wave length[3] was radiated. The closed circuit condensers were of the well-known Fessenden compressed-air type, and for a wave length of 3750 meters the capacity was 0.18 microfarad. The spark gap was of the Fessenden synchronous rotary type with two fixed electrodes and a system of rotary electrodes mounted on the shaft of the generator. The generator was rated at 100 kilowatts at 500 cycles, thus producing 1000 sparks per second. It was not possible to run the generator at full power with the steam engine available at the time of the experiments, the actual power expended being 50 to 60 kilowatts.

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[1] W. Duddell and J. E. Taylor, Electrician, **55**, p. 260; 1905.

[2] C. Tissot, Electrician, **56**, p. 848; 1906.

The scout cruisers were provided with flat top antennas supported by steel masts surmounted by wooden topmasts. The antenna dimensions were: Length 116 feet, breadth 40 feet, number of longitudinal wires 14, cross wires 15. During the December test, the height above the water was approximately 112 feet, but this height was increased in the three later tests to 130 feet. The capacity was about 0.0018 microfarad and the inductance 0.038 millihenry. During the May experiments the capacity of the *Birmingham* was increased by two 70-foot cages forward and two 80-foot cages aft set at an angle of approximately 30° with the vertical. These cages were similar to those forming the umbrella of the Brant Rock tower. This increased the capacity to about 0.0025. In the midst of the July tests, cages were added to the *Salem* also, but the change resulted in no observable variation in the intensity of the signals, the increase in capacity being apparently counterbalanced by the decrease in effective height. The closed circuit was coupled to the antenna, so that but one wave length was radiated, and the closed circuit capacity was 0.036 microfarad at 3750 meters, and 0.018 microfarad at 1000 meters wave length. The motor generators were 500-cycle machines rated at 10 kilowatts, and the spark gap was of the same type as that used at Brant Rock but of smaller dimensions.

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[3] Experience has shown that when the closed circuit is properly designed—that is, without undue waste of energy from brushing, etc.—the greatest range is obtained by a coupling loose enough to give but one wave length in the antenna.

JULY EXPERIMENTS

I_s. Sending antenna current in amperes.
I_R. Received antenna current through 25 ohms.
N. Night observations.
K. Received antenna current at 1 kilometer distance.
d. Distance in kilometers.
h. Height of flat top antenna.
α. Day absorption coefficient $= 0.0015$.
λ. Wave length.
H. Stat. Heavy static = atmospheric discharges preventing reception of signals.
Miles. Nautical mile = 1.85 kilometers.
For good communication. $I_R = 40 \times 10^{-6}$ amperes through 25 ohms $= 4 \times 10^{-8}$ watts.
For audible signals. $I_R = 10 \times 10^{-6}$ amperes through 25 ohms $= 2.5 \times 10^{-9}$ watts.

Preliminary experiments were begun early in July, the scout cruisers lying at anchor in the harbor at Provincetown, 22 miles from Brant Rock. The path of the waves between the ships and the shore station, except for a narrow strip of sand hills bounding Provincetown Harbor, lay entirely over water. Later, when the ships put to sea, it was found that this strip of land made no appreciable difference in the received signals. Careful measurements were made on the intensity of the received antenna current at Brant Rock for the two wave lengths 1 000 meters and 3 750 meters. This current was measured either by means of a hot-wire ammeter of 15 ohms resistance, provided with a mirror for mirror and scale readings,[4] or by a tellurium constantan thermoelement,[5] also of 15 ohms resistance. The hot wire ammeter gave a scale deflection of about 0.2 millimeter for 1 milliampere oscillatory current in the antenna and 9.4 millimeters for 10 milliamperes. One millimeter galvanometer deflection with the thermoelement was equivalent to 263 microamperes, and the deflections were, as nearly as could be determined, directly proportional to the square of the oscillatory current. For the 1000-meter wave length a variable air condenser was placed in series with the Brant Rock antenna, and in this way it was possible to adjust the antenna resistance for both wave lengths to about 25 ohms. From a number of observations it was determined that the received current at Brant Rock for a wave length of 1000 meters was 10 500 microamperes for the *Birmingham*, with a sending antenna current of 33 amperes,[6] and 11 000 microamperes for the *Salem*, corresponding to a sending antenna current of 27 amperes. For a wave length of 3750 meters the received currents were 3200 microamperes for the *Birmingham* and 4100 microamperes for the *Salem*, corresponding to sending antenna currents of 27 and 24 amperes.

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[4] L. W. Austin, Electrical World, **49**, p. 308; 1907.

[5] This Bulletin, **7**, p. 304.

After the ships had attained distances too great to permit the reading of the received signals at Brant Rock by means of thermoelements, a chalcopyrite zinkite rectifier with galvanometer was employed whenever the atmospheric disturbances permitted. This was connected in a secondary circuit coupled to the antenna and calibrated by means of a thermoelement in the antenna and an exciting buzzer circuit which could be tuned to the wave length used.[7]

Throughout the experiments, both at Brant Rock and on shipboard, shunted telephone readings were taken on the incoming signals. The detectors used for the shunt readings were of the free wire electrolytic type and the head telephones connected in series were each of 600 ohms resistance,[8] the shunt being placed across one of these according to the Fessenden method. The circuits for the galvanometer and for the shunt readings at Brant Rock are shown in Fig. 1.

An extended comparison of antenna currents through circuit A and the shunt readings as taken in circuit B was made, and the

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[6] It will be noticed that while the radiation current of the *Birmingham* is considerably greater than that of the *Salem*, the strength of received signal is slightly less. It is possible that the apparently greater radiation of the *Birmingham* was due to a deck insulator which gave trouble throughout the July test. It is not improbable, therefore, that the actual antenna current was not greater than that of the *Salem*. The mean of the readings of the two ships, 30 amperes at a wave length of 1000 meters, has been taken as a basis for calculation.

[7] See this Bulletin, 7, p. 295.

[8] The inductive resistance of each telephone used in calculating the shunt ratio was 2000 ohms.

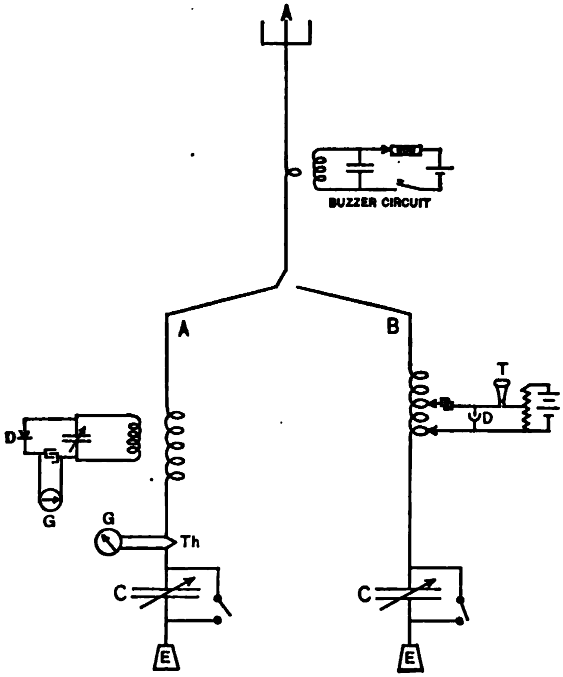

Fig. 1

TABLE I

Shunts on 600-Ohm Telephone with Electrolytic Detector, and Antenna Current Through 25 Ohms

Shunt Ohms	Antenna Current 10^{-6} Amp.	Shunt Ohms	Antenna Current 10^{-6} Amp.
0.5	672	25	95
.6	614	30	87
.7	568	40	76
.8	530	50	68
1.0	474	70	58
2	336	100	49
3	274	150	40
4	237	200	35
5	212	300	29
6	194	400	26
8	168	600	22
10	150	1000	18
12	137	2000	15
15	122	3000	13
20	106	∞	10

results are shown in Table I. The table shows the amount of current in an antenna having a total resistance of 25 ohms which would correspond to the telephone shunt readings on a detector coupled to the antenna with the degree of coupling capable of drawing the maximum amount of energy into the detector.[9]

Shunt readings are very difficult to take even under the best circumstances. In a quiet laboratory it has been found possible to make them agree among themselves with average errors in the single observations not greater than 10 per cent. In a wireless station, with its varying degree of noise, especially if the station is on shipboard, the errors are much greater than this, amounting under ordinary circumstances with good operators to from 20 to 40 per cent; while in a stormy time, or when the atmospheric discharges are heavy, the observed strength of signal will often be only a small fraction of that which would have been observed under normal conditions. It is evident that most of these sources of error tend to decrease the observed value of the signal. Occasionally, however, a loose contact or a loose plug where plug resistance boxes are used, will produce abnormally high values. Then, too, the difference in ear sensitiveness of different operators produces variations in the record. For this reason it is necessary that a very large number of observations be taken to make the results of much value.

As the received currents given in the curves and tables are proportional to the square root of the loudness of signal, the percentage errors are of course smaller than the errors in taking the shunt readings.

The standard of audibility taken in this work is that strength of signal which permits a clear differentiation of the dots and dashes.

The *Birmingham* sailed from Provincetown early on the morning of July 14, taking a course nearly south until she had attained a distance of about 1200 miles from Brant Rock. The *Salem*

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[9] The actual amount of current in the antenna for the same intensity of signal in the detector varies with the effective resistance, which in turn depends on the wave length and amount of tuning inductance. The energy in the detector, required to produce given signals is constant, however. This energy is what is actually measured in taking shunt readings, and for convenience of comparison its square root is put in terms of micro amperes through 25 ohms which was the resistance actually employed in the thermoelement readings at Brant Rock, and which is approximately the effective resistance of a properly coupled ship's antenna of moderate size at a wave length of 1000 meters.

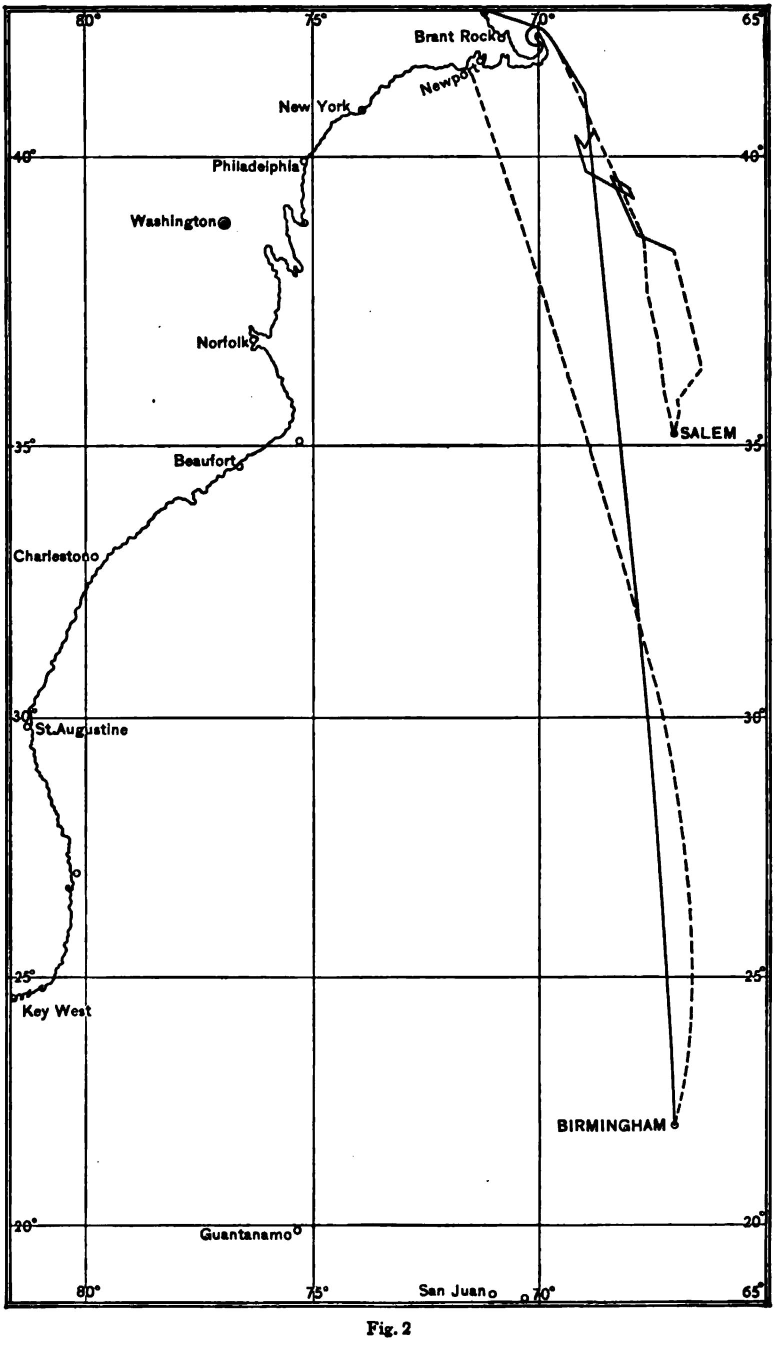
80°
75°
70°
65°
Brant Rock
Newport
New York
Philadelphia
Washington
Norfolk
Beaufort
Charleston
St. Augustine
Key West
SALEM
BIRMINGHAM
Guantanamo
San Juan
40°
35°
30°
25°
20°

Fig. 2

TABLE II

Birmingham Received at Brant Rock

July		λ=1000 M. I_0=33 amp.			July		λ=3750 M. I_0=27 amp.		
		Distance, Nautical Miles	Received Current 10^{-6} amp.				Distance, Nautical Miles	Received Current 10^{-6} amp.	
14	8 a. m.	22	10500	Galvanometer	14	8.30 a. m.	22	3000	Galvanometer
	2 p. m.	50	4600			3.30 p. m.	60	1370	
	8 p. m.	110	N 2100			9.30 p. m.	120	N 520	
15	8 a. m.	256	520		15	9.30 a. m.	266	180	
	2 p. m.	335	157			3.30 p. m.	345	67	
	8 p. m.	415	N 336			9.30 p. m.	425	N 77	
16	8 a. m.	550	77		16	9.30 a. m.	560	49	
	2 p. m.	626	54			3.30 p. m.	636	H. Stat.	
	8 p. m.	702	N 210			9.30 p. m.	712	N 106	
17	8 a. m.	854	H. Stat.		17	9.30 a. m.	864	26	
	2 p. m.	927				3.30 p. m.	937	Stat.	
	8 p. m.	1000	N 19			9.30 p. m.	1010	N 10	
18	8 a. m.	1170	H. Stat.		18	9.30 a. m.	1170		
	2 p. m.	1185	H. Stat.			3.30 p. m.	1185		
	8 p. m.	1200	N 51			9.30 p. m.	1200	N 44	
19	8 a. m.	1152	H. Stat.		19	9.30 a. m.	1152	26	
	2 p. m.	1103	H. Stat.			3.30 p. m.	1103		
	8 p. m.	1035	N 210			9.30	1025	N Not send	
20	8 a. m.	890	35		20	9.30 a. m.	880	26	
	2 p. m.	841	29			3.30 p. m.	831		
	8 p. m.	772	N 240			9.30 p. m.	762	N Not send	
21	8 a. m.	648	26		21	9.30 a. m.	638	26	
	2 p. m.	559				3.30 p. m.	549		
	8 p. m.	470	N 150			9.30	460	N Not send	
22	8 a. m.	320	210		22	9.30 a. m.			
	2 p. m.	240				3.30 p. m.			
	8 p. m.	190				9.30 p. m.			

followed on the morning of July 15 and proceeded slowly to a point about 450 miles from Brant Rock. The courses of the two ships are shown in figure 2. Regular sending and receiving periods were observed at the three stations. At Brant Rock the signals were received as far as possible on the thermoelement and a few readings were taken with the rectifier, but while the preceding week had been almost completely free from atmospheric disturbances, unfortunately, soon after the ships sailed, strong disturbances set in which precluded the possibility of galvanometer measurements, so that for the rest of the experiments all the readings had to be taken by the shunted telephone method. On the ships no attempt was made to use deflection methods, although

TABLE III

Brant Rock Received on Birmingham

July		$\lambda = 1500$ m $I_s = 56$ amp.			July		$\lambda = 3750$ m $I_s = 69$ amp.		
		Distance, Nautical Miles	Received Current 10^{-6} amp.				Distance, Nautical Miles	Received Current 10^{-6} amp.	
15	10.15 a. m.	290		336	15	10.45 a. m.	295		120
	10.15 p. m.	445	N	274		10.45 p. m.	450	N	63
16	10.15 a. m.	580		58	16	10.45 a. m.	585		
	10.15 p. m.	727	N	160		10.45 p. m.	732	N	77
17	10.15 a. m.	885		28	17	10.45 a. m.	890		
	10.15 p. m.	1040	N	106		10.45 p. m.	1045	N	37
18	10.15 a. m.	1180		Stat.	18	10.45 a. m.	1185		
	10.15 p. m.	1215	N	130		10.45 p. m.	1215	N	110
19	10.15 a. m.	1115		Stat.	19	10.45 a. m.	1110		30
	10.15 p. m.	1005	N	106		10.45 p. m.	1000	N	212
20	10.15 a. m.	850		37	20	10.45 a. m.	845		28
	10.15 p. m.	730	N	336		10.45 p. m.	725		Not send
21	10.15 a. m.	600		150	21	10.45 a. m.	595		51
	10.15 p. m.	435	N	194		10.45 p. m.	430	N	54
22	10.15 a. m.	275		390	22	10.45 a. m.	270		Not send
	10.15 p. m.	115	N	336		10.45 p. m.	110		Not send

it is possible that satisfactory measurements could have been taken by means of marine galvanometers. Tables II to VI contain the data of the experiments, the received signals being reduced to terms of current through 25 ohms antenna resistance.

TABLE IV

Salem Received at Brant Rock

July	λ=1000 m I_0=27 amp.		July	λ=3750 m I_0=23 amp.	
	Distance, Nautical Miles	Received Current 10^{-6} amp.		Distance, Nautical Miles	Received Current 10^{-6} amp.
			15 6 a. m.	22	4400
15 5 a. m.	22	11000	9 a. m.	52	1420
8 a. m.	45	5000	3 p. m.	70	1250
2 p. m.	60	3600	9 p. m.	117	N * 613
8 p. m.	117	N 2170			
16 8 a. m.	125	2250	16 9 a. m.	130	693
2 p. m.	105	2275	3 p. m.	110	* 567
8 p. m.	137	N 1328	9 p. m.	140	N * 474
17 8 a. m.	207	* 1062	17 9 a. m.	210	* 274
2 p. m.	190	646	3 p. m.	190	* 500
8 p. m.	196	N 400	9 p. m.	196	N * 179
18 8 a. m.	249	580	18 9 a. m.	250	* 237
2 p. m.	270	520	3 p. m.	275	* 274
8 p. m.	290	N 410	9 p. m.	295	N * 194
19 8 a. m.	366	200	19 9 a. m.	370	* 106
2 p. m.	394	182	3 p. m.	400	* 115
8 p. m.	425	N * 672	9 p. m.	430	Not send
20 8 a. m.	322	325	20 9 a. m.	315	Not send
2 p. m.	254	582	3 p. m.	245	Not send
8 p. m	181	N Stat.	9 p. m.	175	Not send

* Telephone readings

Wherever possible the readings taken by the deflection method are used. During the experiments the atmospheric disturbances were heavy most of the time, especially at night and at the longer wave length. These frequently entirely prevented the reception of the signals as indicated by the blanks in the received current column. No table is given for Brant Rock received on the *Salem*, because during a great part of the time the signals were too strong for accurate shunt readings. No tables are given for the work between the two cruisers at a wave length of 3 750 meters, as their antennas seemed too small to work successfully at this wave length and only a few unsatisfactory shunt readings were obtained.

TABLE V

"Salem" Received on "Birmingham"

July	$\lambda = 1000$ m, $I_o = 27$ Amp.	
	Distance, Nautical Miles	Received Current 10^{-6} Amp.
15 8 a. m.	253	170
2 p. m.	274	196
8 p. m.	312	N 120
16 8 a. m.	420	87
2 p. m.	521	54
8 p. m.	574	N 87
17 8 a. m.	661	21
2 p. m.	750	20
8 p. m.	840	N 30
18 8 a. m.	960	Stat.
2 p. m.	972	Stat.
8 p. m.	960	N 46
19 8 a. m.	828	10
2 p. m.	720	26
8 p. m.	618	N 46
20 8 a. m.	589	43
2 p. m.	566	54
8 p. m.	555	N 69
21 8 a. m.	666	46
2 p. m.		
8 a. m.		

TABLE VI

"Birmingham" Received on "Salem"

July	$\lambda = 1000$ m, $I_o = 33$	
	Distance, Nautical Mile	Received Current 10^{-6} Amp.
15 8.30 a. m.	256	160
2.30 p. m.	278	150
8.30 p. m.	315	N 105
16 8.30 a. m.	425	60
2.30 p. m.	526	43
8.30 p. m.	579	N 63
17 8.30 a. m.	666	H. Stat.
2.30 p. m.	755	H. Stat.
8.30 p. m.	845	N 38
18 8.30 a. m.	960	10
2.30 p. m.	972	10
8.30 p. m.	960	N 10
19 8.30 a. m.	823	10
2.30 p. m.	715	Stat.
8.30 p. m.	613	N 77
20 8.30 a. m.	584	38
2.30 p. m.	561	38
8.30 p. m.	555	Messages
21 8 30 a. m.	661	38

For determining the law of the decrease of the intensity of the signal with the distance a smooth curve was drawn through the observed day readings and points on this were taken as the

TABLE VII

Birmingham Received at Brant Rock, July

		I_S = 33 amp. λ = 1000 m. K = 475000 10^{-6} amp.			I_S = 27 amp. λ = 3750 m. K = 138000 10^{-6} amp.		
Nautical Miles	d Km	$\frac{K}{d}$ 10^{-6} amp.	I_R 10^{-6} amp.		$\frac{K}{d}$ 10^{-6} amp.	I_R 10^{-6} amp.	
			Obs.	Cal.		Obs.	Cal.
20	37	12830	11500	12200	3730	3500	3620
50	92.5	5135	4600	4460	1492	1400	1385
100	185	2565	2100	1940	746	700	645
200	370	1283	800	737	373	260	280
300	555	856	260	370	249	120	161
400	740	642	130	212	187	60	105
500	925	514	80	128	149	40	73
600	1110	428	50	81.5	124	30	52
800	1480	321	35	35	93	24	29
1000	1850	257	20	15.4	75	22	18

TABLE VIII

Brant Rock Received on Birmingham, July

		I_S = 56 amp. λ = 1500 m K = 310000.10^{-6} amp.			I_S = 69 amp. λ = 3750 m K = 160000.10^{-6} amp.		
Nautical Miles	d Km	$\frac{K}{d}$ 10^{-6} amp.	I_R 10^{-6} amp.		$\frac{K}{d}$ 10^{-6} amp.	I_R 10^{-6} amp.	
			Obs.	Cal.		Obs.	Cal.
20	37	8380		8000	4325		4200
50	92.5	3350		2980	1730		1610
100	185	1675		1340	865		750
200	370	838		533	432		324
300	555	558	320	283	288	120	187
400	740	419	160	170	216	85	121
500	925	335	80	108	173	65	84.5
600	1110	279	52	72.5	144	52	60.8
800	1480	209	38	34.7	108	40	34.1
1000	1850	167	25	17.1	87	30	20.6

observed values for purposes of calculation. It was assumed from the results of Duddell and Taylor and Tissot that the received currents would be inversely proportional to the distance provided no absorption existed. The observed curve indicated that this was approximately true up to a point between 100 and 200 miles, but beyond this point the currents evidently dropped much more rapidly. The simplest assumption in regard to absorption is that it is proportional to the distance. Joining this to the Duddell and Taylor law we have as an expression for the received current

$$I_R = \frac{K}{d} e^{-Ad} \qquad (1)$$

where d is the distance, K the received current at unit distance, e the base of the natural logarithms, and A a constant. Dr. Louis Cohen of the National Electric Signaling Co., while testing the validity of this formula made the discovery that A was inversely proportional to the square root of the wave length within the limits of accuracy of the observations. Then, writing $A = \frac{\alpha}{\sqrt{\lambda}}$ the expression becomes

$$I_R = \frac{K}{d} e^{-\frac{\alpha d}{\sqrt{\lambda}}} \qquad (2)$$

α is the absorption coefficient and in these experiments equals 0.0015, the distance and wave length being expressed in kilometers.

Tables VII to XI contain a comparison of the calculated values with those taken from the smoothed observation curves. It is seen that the agreement is exceedingly good in the case of the signals between the *Birmingham* and the *Salem* and those of the *Salem* received at Brant Rock. In the case of the signals between Brant Rock and the *Birmingham*, however, the observed values fall somewhat below the calculated, from 300 to 600 miles. As the observed curve has the same form both for the signals received on the *Birmingham* and those received at Brant Rock the divergence is probably not accidental, and is probably due to a temporary increase of absorption accompanying a marked change in the weather at about this time. The effect is not observed in the *Salem* signals received at Brant Rock because the *Salem* at this time had not attained a great enough distance to make the absorption play an important part.

TABLE IX

"Salem" Received at Brant Rock, July

Nautical Miles	d Km	$I_S = 27$ Amp. $\lambda = 1000$ m $K = 490000\ 10^{-6}$ Amp.			$I_S = 23$ Amp. $\lambda = 3750$ m $K = 170000\ .10^{-6}$ Amp.		
		$\frac{K}{d}$ 10^{-6} Amp.	I_R 10^{-6} Amp.		$\frac{K}{d}$ 10^{-6} Amp.	I_R 10^{-6} Amp.	
			Obs.	Cal.		Obs.	Cal.
20	37	13250	12000	12500	4595	4500	4460
50	92.5	5300	4700	4610	1838	1800	1710
100	185	2650	2200	2000	919	850	800
150	278	1760	1200	1170	612	500	495
200	370	1325	750	760	459	330	344
300	555	883	370	382	306	190	198
400	740	662	200	218	230	115	129
500	925	530	130	132	184	88	90

TABLE X

Salem Received on Birmingham, July

Nautical Miles	d Km	$I_s = 27$ amp. $\lambda = 1000$ m. $K = 230000\ 10^{-6}$ amp.		
		$\frac{K}{d}$ 10^{-6} amp.	I_R 10^{-6} amp.	
			Obs.	Cal.
20	37	6220		5880
50	92.5	2486		2160
100	185	1243		941
200	370	622	325	357
300	555	414	165	179
400	740	311	95	102
500	925	249	65	62
600	1110	207	45	39.4
800	1480	155	19	17.1
1000	1850	124	10	7.5

TABLE XI

Birmingham Received on Salem, July

Nautical Miles	d Km	$I_s = 33$ amp. $\lambda = 1000$ m. $K = 185000\ 10^{-6}$ amp.		
		$\frac{K}{d}$ 10^{-6} amp.	I_R 10^{-6} amp.	
			Obs.	Cal.
20	37	5000		4730
50	92.5	2000		1740
100	185	1000		757
200	370	500	260	287
300	555	333	130	144
400	740	250	75	82.4
500	925	200	50	49.9
600	1110	167	35	31.7
800	1480	125	16	13.8
1000	1850	100	10	6.2

The curves of figures 3 to 10 give the results in graphic form. The dotted line gives the strength of signal which would have been received if the K/d law had obtained; that is, if there had been no absorption. The continuous curve gives the theoretical day values as calculated from equation 2, while the individual observations are represented by crosses. Observations taken by the deflection method are indicated by circles around the crosses, while night observations are accompanied by the letter N. It is seen that the day observations correspond approximately to the values of the calculated curve, but that the night signals are entirely irregular,

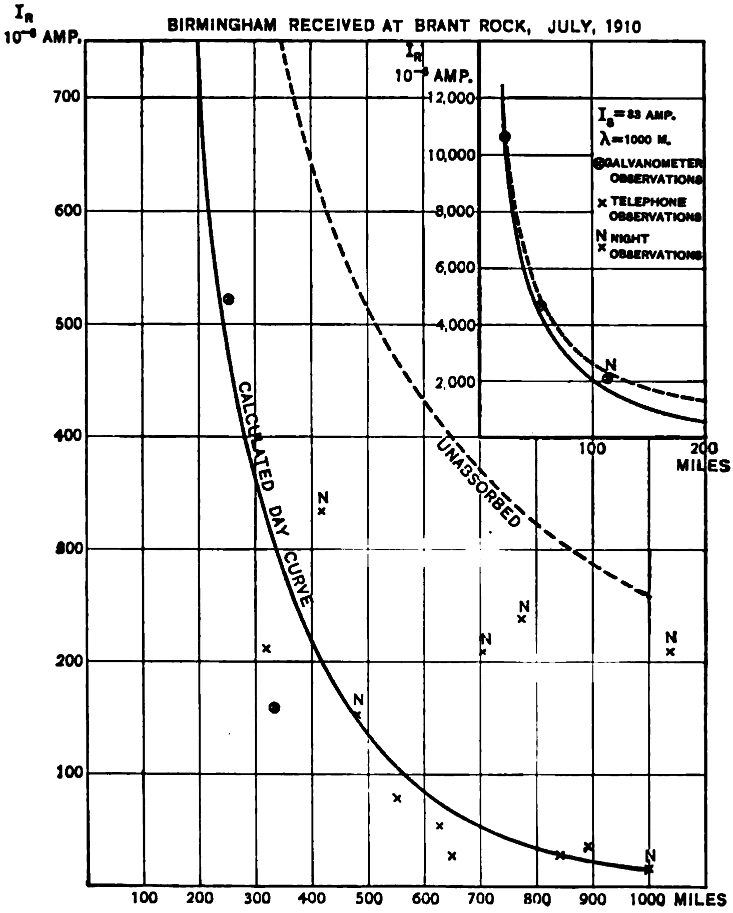

Fig. 3

being in general stronger than the day signals, as was first observed by Marconi. Sometimes they lie close to the K/d curve, indicating that the absorption has disappeared, while at others they are practically of the same strength as the day readings. In a very few cases, night signals were observed considerably stronger than the calculated value for zero absorption, but these may very probably be due to errors of observation, since it is not observed that the remarkable strength of signal is reciprocal between the two stations. If the observations are genuine, however, it would perhaps indicate some kind of reflection from the upper layers of the atmosphere.

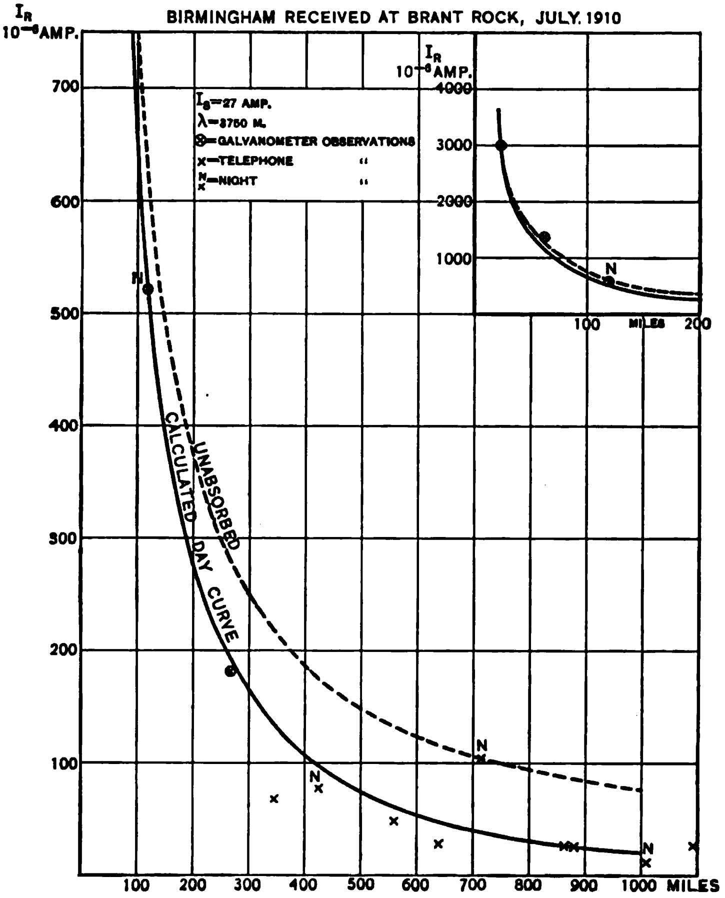

Fig. 4

THE CAUSE OF THE ABSORPTION

According to the calculations of Zenneck,[10] the conductivity of air at moderate heights can not explain the magnitude of the observed absorption, neither can the sea-water absorption be of the proper magnitude, according to the same author. But as the wave front at any considerable distance from the sending station must extend far into the upper layers of the atmosphere, it does not seem improbable that this is the region of absorption. If

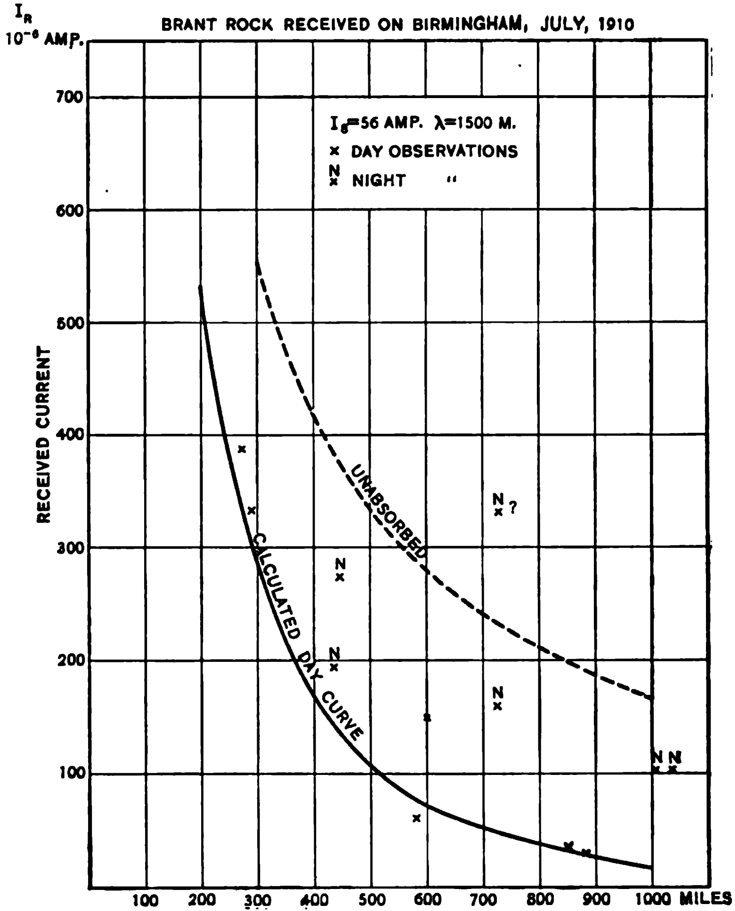

Fig. 5

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[10] Zenneck, Ann. d. Phys., **28**, p. 846; 1907.

the conductivity is increased by the sun's rays at these heights, this would also explain the differences in the strength of the day and night signals. The observations would indicate, if this explanation is true, that the excessive ionization may, especially in summer, persist through many nights. The general experience of wireless telegraphy would indicate that during the colder months the absorption dies out more uniformly at night. The day absorption appears from the data obtainable to be fairly uniform

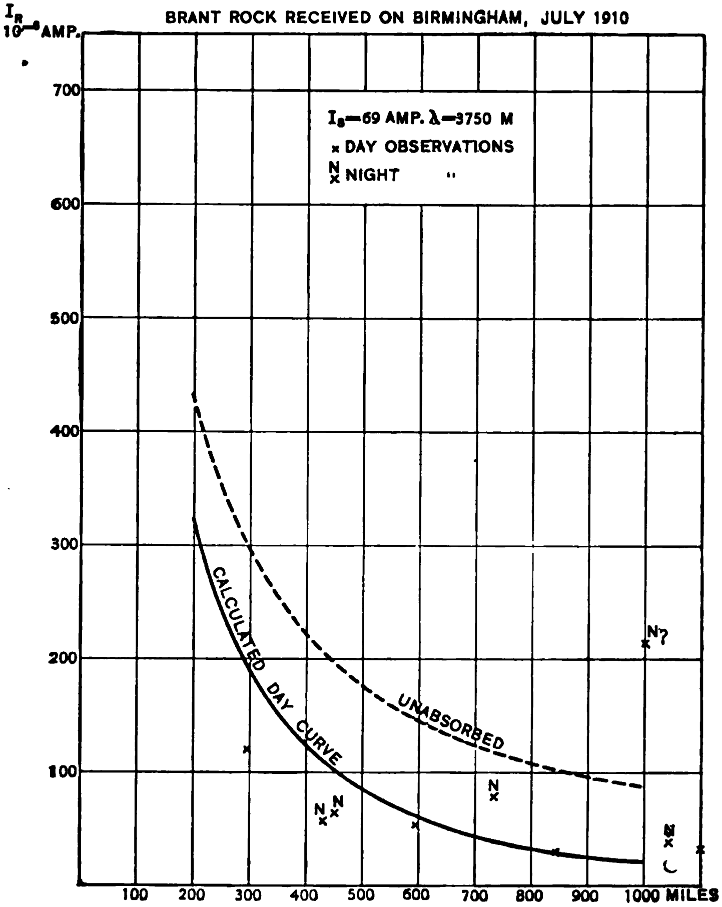

Fig. 6

throughout the year, at least in the portion of the ocean covered by our observations, although there are undoubtedly variations at times, as has been already mentioned in regard to the *Birmingham*-Brant Rock signals. There are well-authenticated instances when, for a day or two, the absorption seems to nearly disappear in the daytime. A case in point is that of the long-distance day signals between the *Birmingham* and Brant Rock on the return voyage from Liberia mentioned on page 351.

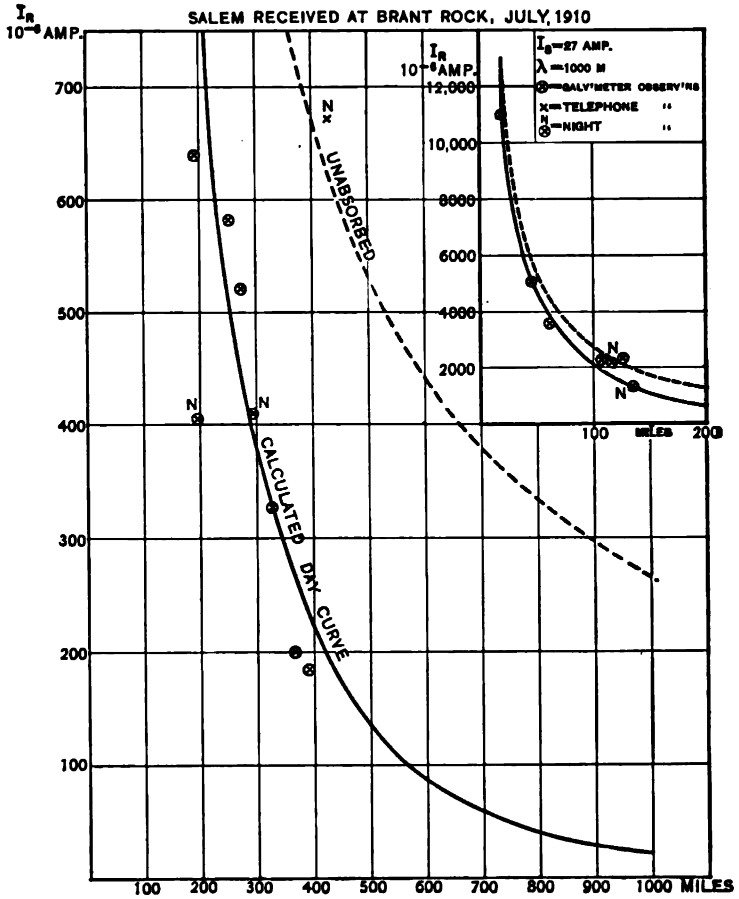

Fig. 7

SUPPLEMENTARY MEASUREMENTS

PROPORTIONALITY OF SENDING AND RECEIVING CURRENTS

It was thought possible that when the antennas were used with the highest power, especially at the longer wave lengths, there might be losses of energy, either by brushing or by leakage over the insulators, which might destroy the proportionality between sending antenna current and received antenna current. To settle this question, the station at Brant Rock sent with varying powers at a wave length of 3750 meters. The signals were received on the antenna at the Bureau of Standards at Washington, D. C.,

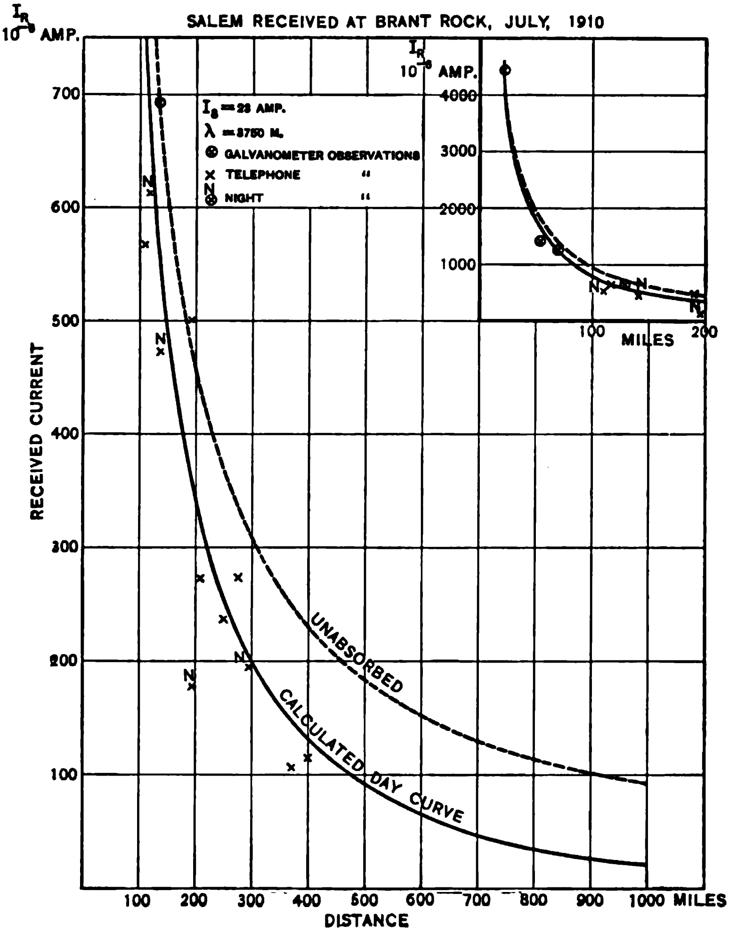
SALEM RECEIVED AT BRANT ROCK, JULY, 1910

Fig. 8

380 miles away. The receiving antenna was of the harp form, 180 feet high at top, 40 feet high at bottom, and 18 feet wide, with 8 wires. The capacity was approximately 0.0012 microfarad. A chalcopyrite zinkite rectifier, with a sensitive galvanometer, was connected in a tuned secondary circuit coupled to the antenna inductance so as to give maximum deflection, the circuits being those shown under circuit A in Fig. 1. The results are shown in the curve of Fig. 11. The galvanometer deflections are proportional to the square of the current, hence the square roots of the deflections expressed in microamperes of received antenna current are compared with the sending antenna current at Brant Rock.

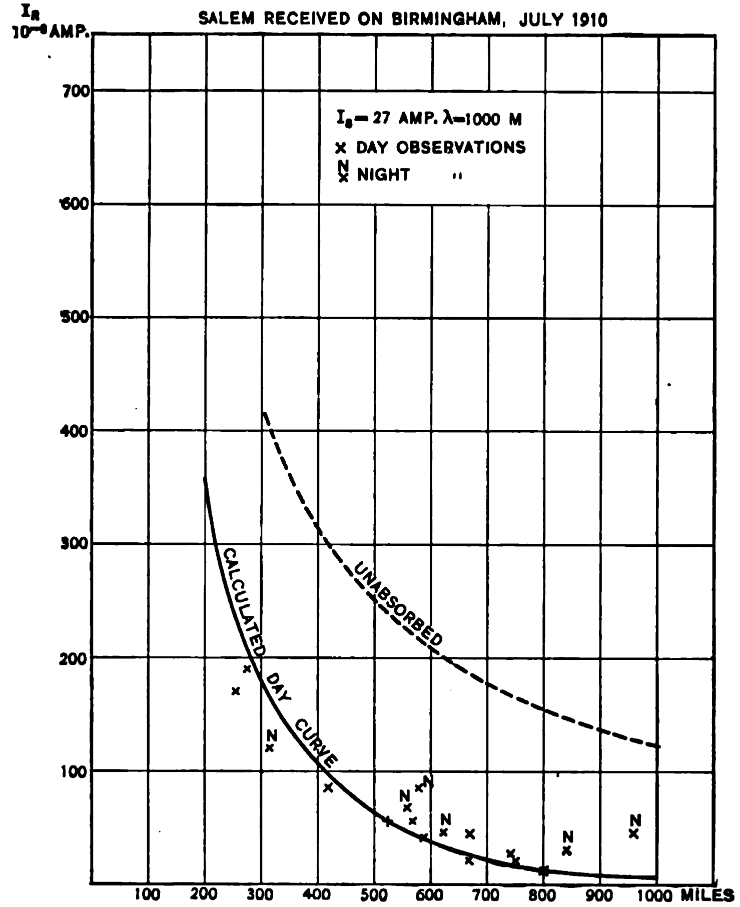

Fig. 9.

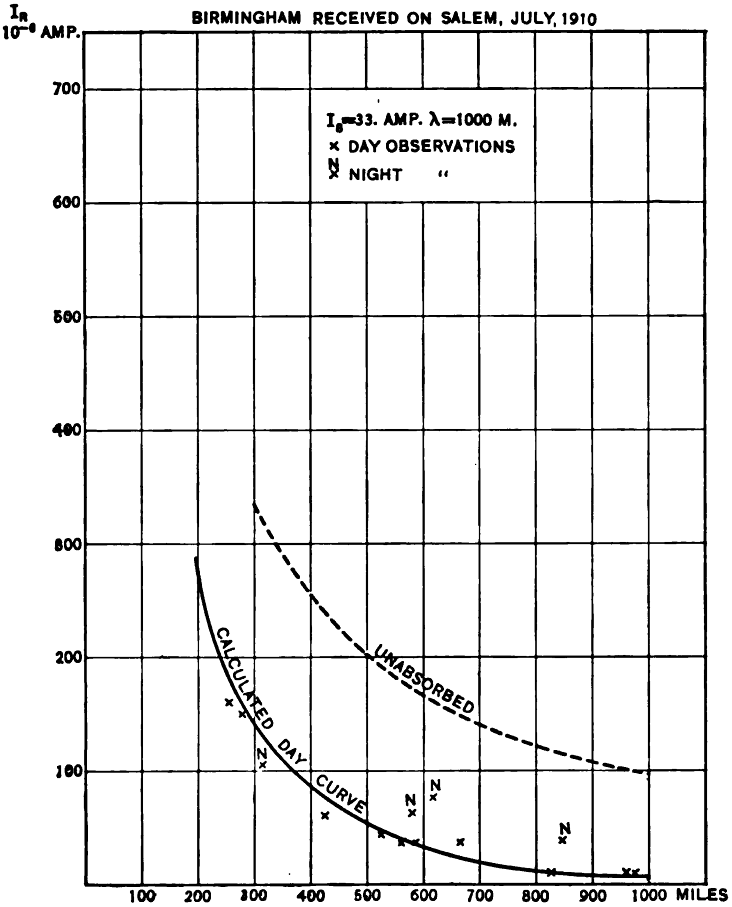
BIRMINGHAM RECEIVED ON SALEM, JULY, 1910
I_R 10^{-6} AMP.
700
600
500
400
300
200
100
I_S=33. AMP. λ=1000 M.
× DAY OBSERVATIONS
N × NIGHT "
UNABSORBED
CALCULATED DAY CURVE
100 200 300 400 500 600 700 800 900 1000 MILES

Fig. 10

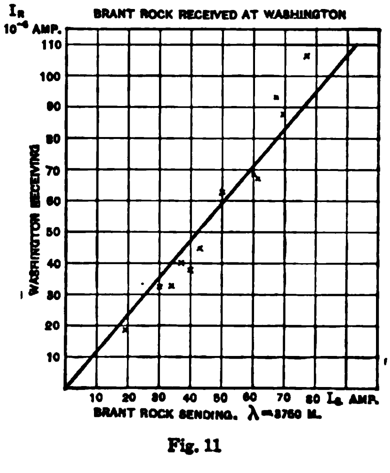
BRANT ROCK RECEIVED AT WASHINGTON
I_R 10^{-6} AMP.
110
100
90
80
70
60
50
40
30
20
10
WASHINGTON RECEIVING
10 20 30 40 50 60 70 80 I_S AMP.
BRANT ROCK SENDING. λ=3750 M.

Fig. 11

The proportionality is fairly good. It is possible that in the changes of adjustment of the circuits at Brant Rock the tuning became somewhat deranged, or that the change of the coupling at Brant Rock produced a change in the damping of the waves, which was not compensated for by a change in the coupling at Washington. A few observations were taken at Brant Rock on signals sent from the *Birmingham* when coming into Newport, R. I., both at wave lengths of 1000 meters and 3750 meters. From these it was concluded that there was no marked overloading of the sending antenna, although there were slight indications in this direction at the wave length of 3750 meters.

THE EFFECT OF ANTENNA HEIGHT AND WAVE LENGTH IN SENDING AND RECEIVING

At the close of the test with the scout cruisers, a flat top antenna was erected at Plymouth, 11 miles from Brant Rock, for the purpose of investigating the relationship of height of antenna and wave length to sending and receiving. Except for a narrow sand spit the whole path of the waves between the two stations lay over water. The antenna was swung between two noninsulated steel masts in order to reproduce as fully as possible the conditions on board ship. The Plymouth antenna had a length of 110 feet and consisted of 11 wires 2 feet apart. The capacity was approximately 0.001 microfarad. The Plymouth station was furnished with a 2-kilowatt, 500-cycle Fessenden sending set, and a somewhat larger 500-cycle set used at Brant Rock. The currents were measured at both stations by means of 15-ohm thermoelements with galvanometers as described on page 317. The experiments were begun by my assistants, but were completed by Dr. Cohen of the National Electric Signalling Co.

SENDING

Table XII gives the results of observations taken by Dr. Cohen and his assistants, Plymouth being the sending station and Brant Rock the receiving. This table is for the most part self-explanatory. The deflections of the galvanometer connected to the thermoelement are proportional to the square of the current, so that the square roots of these deflections are taken as proportional to the current itself. The deflections are in arbitrary units. For comparison, the square roots of the deflections were reduced to a uniform sending antenna current. These values are given under I_R in the next to the last column, while the last column gives this quantity divided by the height. Although there is considerable

TABLE XII

Plymouth Received at Brant Rock

$\lambda = 3900$ m

Antenna Plymouth h	I_S	Deflection Receiving D	$I_R = \sqrt{D}$ reduced to $I_S = 4.7$ amp.	$\frac{I_R}{h}$
80 ft.	4.7 amp.	62.3	7.9	0.099
70	4.6	34	5.95	.085
60	4.7	30.3	5.5	.092
50	4.85	24.1	4.76	.095
40	4.9	15.6	3.79	.095
30	5.1	7.4	2.51	.084

$\lambda = 1585$ m[1]

h	I_S	D	I_R ($I_S = 5.5$ amp.)	$\frac{I_R}{h}$
70 ft.	5.5 amp.	292	17.1	0.244
60	5.5	198	14.1	.235
50	5.65	110.7	10.2	.204
40	6.05	84	8.32	.207
30	6.3	62	6.88	.229

h = 80 ft.
35 ohms added in receiving antenna

λ	I_S	D	I_R ($I_S = 4.2$ amp.)	$I_R \times \lambda$
3900 m.	4.2 amp.	4.0	2.0	7800
2980	4.5	8.3	2.69	8030
2400	4.75	13.6	3.26	7830
1985	5.1	26.3	4.22	8400

Shorter wave lengths were not used on account of the long natural wave length of the Brant Rock station.

variation in the values of this column it is evident that there is no systematic variation, and for the individual wave lengths we must consider that the received current is proportional to the height of the sending flat-top antenna. The receiving antenna was tuned by means of a variable inductance in series with the thermoelement.

In the last section of Table XII the results show the variation with wave length, and in this case the equivalent received current is multiplied by the wave length and the product is seen to be approximately constant. Thirty-five ohms was introduced into the receiving antenna to nullify the changes in the resistance of the inductance during the process of tuning. This table shows that the received antenna current is proportional to the height of the sending attenna and inversely proportional to the wave length.

RECEIVING

Table XIII gives similar data in regard to the Plymouth antenna used for receiving, the sending station being Brant Rock. This table shows that the same relationship holds for receiving as for sending; that is, for a constant sending antenna height and current the received current is proportional to the height of the receiving antenna and inversely proportional to the wave length.[11]

While it appears that the sending and receiving relations for a flat-top antenna are reciprocal, this is apparently not the case for an umbrella antenna. It is seen from the observations that the scout cruisers, sending with 10 kilowatts, were received at Brant Rock with almost the same strength as that with which Brant Rock, sending with 60 kilowatts, was received on the cruisers. Comparing the strength of the sending and receiving currents, it appears that the umbrella antenna at Brant Rock for sending is only equivalent to a flat-top antenna 170 feet high, which is not far from the height of the lower ends of the umbrella, while for receiving its equivalent height is much greater. A few experiments have also been made on an umbrella and flat top at Plymouth, which also showed that an umbrella is a better receiver than radiator.

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[11] This will not strictly hold in the case where the radiation resistance of the receiving antenna is comparable with the rest of the antenna resistance. See R. Ruedenberg, Ann. d. Phys., **25**, p. 446; 1908.

TABLE XIII

Brant Rock Received at Plymouth

$\lambda = 4000$ m

Antenna Plymouth h	I_S	Deflection Receiving D	$I_R = \sqrt{D}$ reduced to $I_S = 7.0$ amp.	$\frac{I_R}{h}$
80 ft.	7.0 amp.	8.4	2.90	0.0362
70	10.0	12.4	2.46	.0352
60	9.4	8.0	2.10	.0350
50	9.75	6.0	1.76	.0352

$\lambda = 1980$

h	I_S	D	I_R ($I_S = 7.4$ amp.)	$\frac{I_R}{h}$
80 ft.	7.4 amp.	26.0	5.1	0.0637
70	7.6	24.0	4.77	.0682
60	11.1	41.1	4.28	.0713
50	10.9	22.6	3.22	.0644
40	10.4	15.5	2.80	.0700

$h = 70$ ft.
35 ohms added in receiving-antenna

λ	I_S	D	I_R ($I_S = 10$ amp.)	$I_R \times \lambda$
4000 m	10.0 amp.	4.3	2.07	8300
3550	9.1	4.8	2.41	8560
2980	8.6	6.0	2.85	8500
2510	9.9	12.9	3.63	9110
1984	7.6	10.0	4.16	8240

Uniting the experimental data contained in the last two tables with the data obtained from the experiments with the cruisers, we may write an equation which will cover the normal day received current over salt water through 25 ohms for two stations with flat-top antennas of any height, with any value of sending current and any wave length, provided the sending station is so coupled as to give but one wave length.

We may write this equation as follows:

$$I_R = 4.25 \frac{I_S h_1 h_2}{\lambda d} e^{-\frac{\alpha d}{\sqrt{\lambda}}} \tag{3}$$

where I_R represents the current received through 25 ohms resistance, I_S the sending current, h_1 the height of one antenna, h_2 that of the other, d, the distance between the stations, and λ the wave length, where all the lengths are taken in kilometers and the currents in amperes. α is the absorption coefficient, which in our experiments was found to be equal to 0.0015. This disregarding the absorption term $e^{-\frac{\alpha d}{\sqrt{\lambda}}}$, corresponds in form to the Herzian equation for the electromotive force in a vertical resonator at a distance from the oscillator.

TABLE XIV

Calculated Relation between Antenna Current and Distance for Two Ships with Antenna Heights of 130 Feet

$\lambda = 1000$ m

Antenna Current I_S	Working Distance 40.10^{-6} amp.		Extreme Distance of Audibility 10.10^{-6} amp.	
	Day	Night (Zero Absorption)	Day	Night (Zero Absorption)
1 amp.	75 miles	90 miles	200 miles	360 miles
2	135	180	300	720
3	180	270	375	1080
5	235	450	475	1800
7	280	630	550	2520
10	345	900	630	3600
15	420	1350	725	5400
20	475	1800	790	7200
25	525	2250	840	9000
30	565	2700	900	10800
40	630	3600	970	14400
50	685	4500	1025	18000
60	725	5400	1150	21600

In our formula the constant 4.25 applies strictly only to ship antennas with the same losses due to masts, rigging, etc., both in sending and receiving, as found on the scout cruisers. On other ships the value of the constant might probably differ by as much as 30 per cent under ordinary conditions. This difference in the value of the constant does not, however, make a very great difference in the range of communication, although for short distances it would make a considerable difference in the loudness of signal. To show the variation in range of communication with different antenna currents, Table XIV is given, showing the range of communication between two flat top antennas 130 feet high at a wave length of 1000 meters for various values of the sending antenna current, assuming that 40×10^{-6} ampere assures good communication. A quarter of the indicated current would produce audible signals under favorable conditions. The table shows how very slowly the range increases with increasing sending current. Increasing the current from 30 to 60 amperes increases the distance only from 565 miles to about 725 miles, while even with 10 amperes, corresponding to a moderately efficient 2-kilowatt set, 345 miles is easily reached.

In columns 3 and 5 are given the distances attainable for regular communication and audibility on the assumption that there is no atmospheric absorption; that is, the extreme range of night communication.[12]

TABLE XV

Good Working Distance and Sending Current for Two Stations with Flat Top Antennas 450 Feet High

Nautical Miles	$\lambda = 1000$ m	$\lambda = 2500$ m	$\lambda = 3750$ m	$\lambda = 6000$ m
1000	15 amp.	13.5 amp.	15 amp.	17 amp.
1250	38	27	27	30
1500	91	49	44	46
1750	200	95	77	74
2000	490	155	122	105
2250		245	200	160
2500		470	314	235
2750			500	335
3000			775	500

In Table XV is given the estimated day range of two large stations with flat-top antennas 450 feet high for various antenna currents and four wave lengths. The table shows the great advantage of long wave lengths for very distant stations. It is seen that for good communication at a distance of 2500 miles not less than 240 amperes[13] must be used at a wave length of 6000 meters, though one-fourth of this would be audible.

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[12] Excluding the possibility of the effects of reflection from the upper atmosphere.

For the purpose of easily calculating the probable day working distance for various sending currents, heights, and wave lengths according to equation (3) Tables XVI and XVI-A are given. Table XVI gives the current which may be expected to be received through 25 ohms for an antenna height at both stations of 130 feet and a sending antenna current of 30 amperes. Table XVI-A gives the sending currents which will be required for various heights of the sending and receiving antennas h_1 and h_2 to give the values of the received currents as shown in Table XVI. To determine the current which will be received for any antenna height, wave length, and distance for a given sending current, multiply the value, given in Table XVI for the given distance and wave length, by the given current, divided by the value of I_S in Table XVI-A for the given antenna heights.[14] In Table XVI it may be assumed that 40×10^{-6} ampere insures good communication and that 10×10^{-6} ampere is just audible.

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[13] From the experience of the Marconi transatlantic stations it would appear possible that for the same antenna current the distances given in the table could be obtained with a smaller antenna height provided a bent antenna were used.

[14] Example: If $h_1 = 200$ feet, $h_2 = 130$ feet, $\lambda = 600$ meters, distance $= 500$ miles, and $I_S = 12$ amperes, then $I_R = 60.2 \times 12/19.5 = 37.0 \times 10^{-6}$ ampere. The above tables have been given in this convenient form for calculation largely with the hope that they will be tested by the experience of the various wireless companies. It is very common in wireless stations to have an antenna meter for the measurement of the sending current. When this is used with a shunt, the multiplying value of the shunt for the given frequency may easily be obtained by connecting a like unshunted hot-wire meter in the antenna in series with the regular instrument and sending with reduced power so that the needle of the unshunted meter just remains on the scale. The ratio of the readings of the two meters then gives the multiplying value. When only one meter is available an approximate calibration may be obtained by sending with reduced power and observing the reading of the meter without the shunt and then with the shunt connected. Of course this calibration must be carried out with the same wave length used in regular work. The range of good daylight communication with another flat-top antenna of known height over sea water can be compared with the values in the table for the given wave length, distance, and sending current, provided the sending station radiates but a single wave length. If the equation is correct, the tables should indicate a current of from 20 to 40 microamperes.

TABLE XVI

Currents in Microamperes Received Through 25 Ohms for a Sending Current of 30 Amperes and Sending and Receiving Flat Top Antenna Heights of 130 Feet, over Salt Water

[Calculated from Eq. 3]

Nautical Miles	d Km	$\lambda=300$ m		$\lambda=600$ m		$\lambda=1000$ m		$\lambda=1500$ m		$\lambda=2500$ m		$\lambda=3750$ m		$\lambda=6000$ m	
		$K=6.67.10^5$		$K=3.33.10^5$		$K=2.10^5$		$K=1.33.10^5$		$K=8.10^4$		$K=5.33.10^4$		$K=3.33.10^4$	
		$\frac{K}{d}$	I_R	$\frac{K}{d}$	I_R	$\frac{K}{d}$	I_R	$\frac{K}{d}$	I_R	$\frac{K}{d}$	I_R	$\frac{K}{d}$	I_R	$\frac{K}{d}$	I_R
20	37	18000	16300	9000	8350	5400	5100	3590	3430	2160	2080	1440	1400	900	880
50	92.5	7200	5600	3600	3020	2160	1880	1435	1282	864	790	576	536	360	340
100	185	3600	2170	1800	1270	1080	817	720	573	431	361	288	249	180	161
200	370	1800	650	900	433	540	310	359	228	216	152	144	108	90	71.8
300	556	1200	263	600	205	360	156	240	122	144	85	96	62.4	60	42.7
400	740	900	116	450	107	270	89	180	73	108	53.6	72	40.8	45	28.6
500	925	720	55.4	360	60.2	216	53.8	144	46.3	86.4	35.9	57.6	28.2	36	20.5
600	1110	600	27.6	300	34.8	180	34.2	120	31.1	72	25.3	48	20.4	30	15.2
800	1480	450	7.72	225	12.8	135	14.7	90	14.8	54	13.1	36	11.5	22.5	9.06
1000	1850	360	2.27	180	4.97	108	6.7	72	7.5	43.1	7.42	28.8	6.77	18	5.80
1200	2220	300	0.66	150	2.0	90	3.24	60	3.95	36	4.36	24	4.34	15	3.89
1500	2780	240	0.12	120	0.54	72	1.10	48	1.58	28.8	2.04	19.2	2.25	12	2.18
2000	3700	180	0.0081	90	0.069	54	0.205	36	0.385	21.6	0.64	14.4	0.817	9	0.928
2500	4630	144	....	72	0.0086	43.2	0.038	24.8	0.098	17.3	0.213	11.5	0.318	7.2	0.418
3000	5560	120	....	60	0.0010	36	0.0079	24	0.031	14.4	0.073	9.1	0.129	6.0	0.198

TABLE XVI-A

Sending Currents Required to Produce Received Currents as Given in Table XVI for Various Antenna Heights

$h_1=h_2$	I_S amp.	$h_1=450$ ft.		$h_1=200$ ft.		$h_1=130$ ft.		$h_1=100$ ft.	
		h_2	I_S amp.	h_2	I_S amp.	h_2	I_S amp.	h_2	I_S amp.
32.5 ft.	480	32.5 ft.	34.5	32.5 ft.	78	32.5 ft.	120	32.5 ft.	156
65	120	65	17.3	65	39	65	60	65	78
100	51	100	11.3	100	25.3	100	39	130	39
130	30	130	8.7	130	19.5	160	24.4	160	31.8
160	19.8	160	7.1	160	15.8	200	19.5	200	25.4
200	12.7	200	5.6	300	8.5	300	13	300	16.9
300	5.66	300	3.76	450	5.65	450	8.7	450	11.3
450	2.5								

OTHER LONG-DISTANCE WORK

In all of the experiments with the cruisers excepting those carried on during the month of July the calculated received currents at unit distance were estimated from the ratio of the sending currents to those observed at the corresponding stations in July, account of course being also taken of the change in antenna heights on the cruisers from 112 feet to 130 feet after the close of the December tests. This calculation is somewhat arbitrary, since there were many changes in the arrangement of the apparatus which very probably had an influence on the efficiency of the sets. Taking

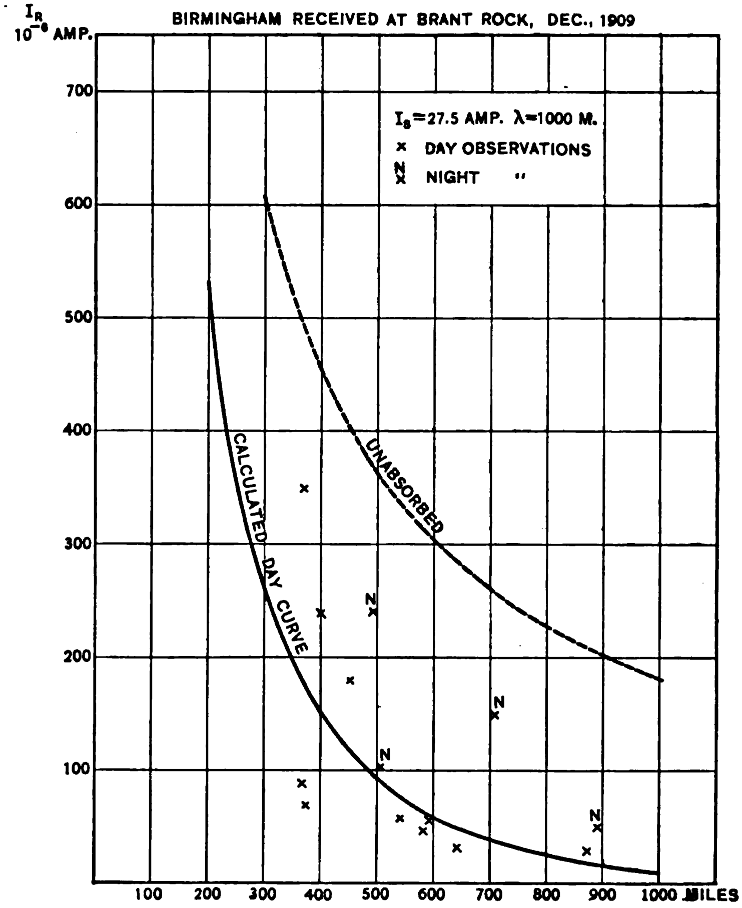

Fig. 12

all this into account, the results of these earlier tests can not by any means be considered to have the same weight as those in July. But as it is desirable to obtain all the light possible on the validity of the transmission formula, the following observations are given.

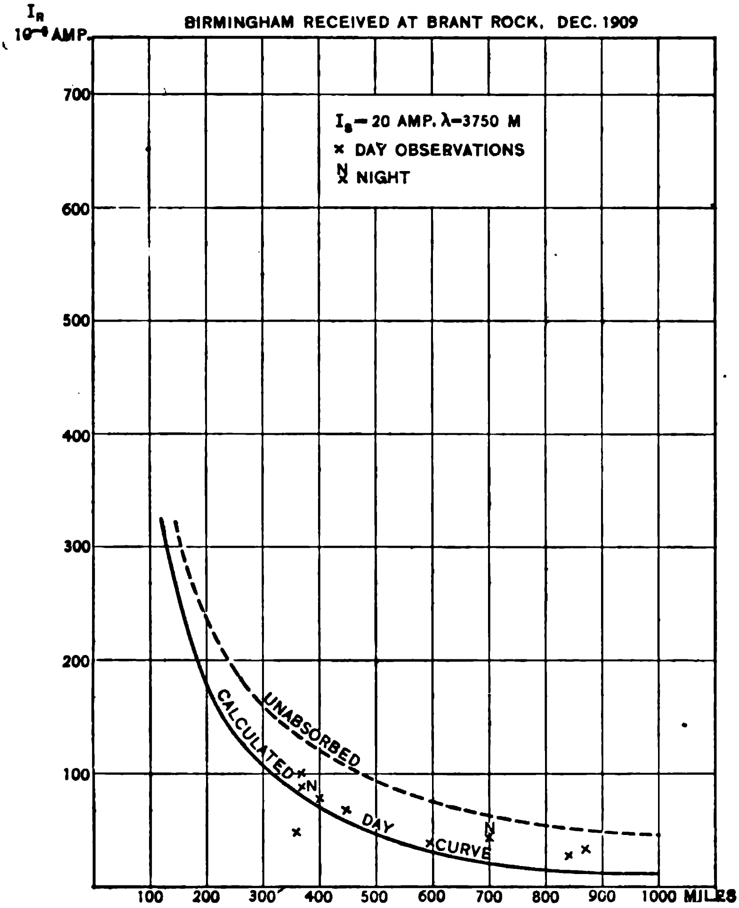

Fig. 13

DECEMBER EXPERIMENTS

The December experiments were made shortly after the installation of the sets on the cruisers, the *Birmingham* taking an easterly course from Provincetown, while the *Salem* sailed to the southward. At the greatest distance attained the two ships were distant from each other and from Brant Rock approximately 1000 miles.

The arrangement of the apparatus on the cruisers was highly unsatisfactory, largely on account of lack of space. In addition to this the weather was extremely tempestuous much of the time. In the light of all this, it is not surprising that the observed received currents fell below the calculated values.

The results are shown in the curves of Figs. 12 to 19.[15]

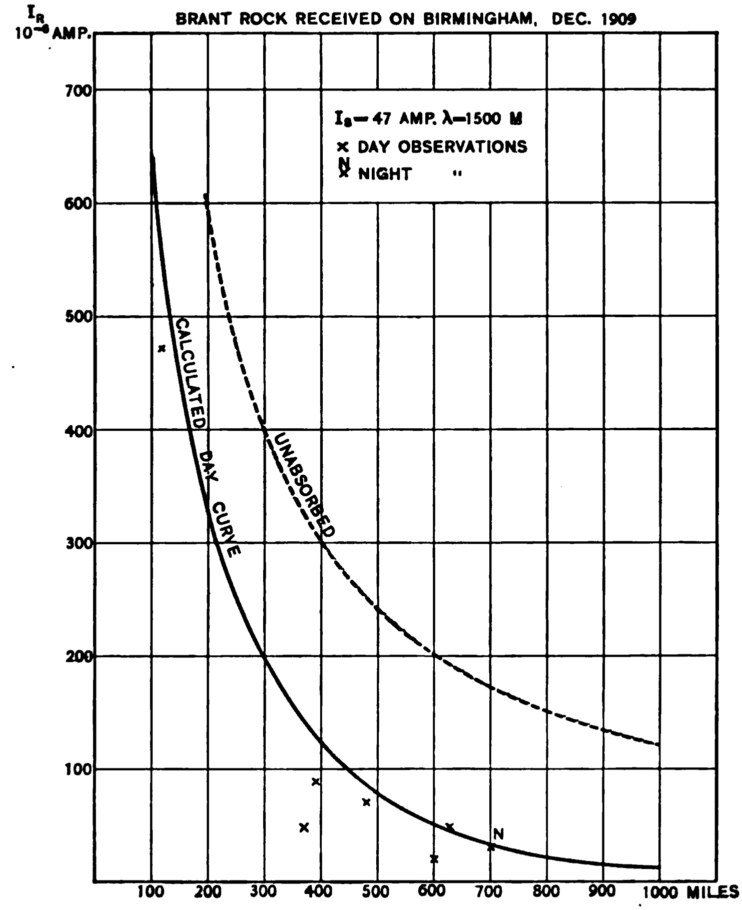

Fig. 14

MARCH EXPERIMENTS

In March the *Birmingham* was sent to Liberia, and during the voyage current measurements were made on the ship and at Brant Rock. The results are shown in Figs. 20 to 23.

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[15] Neither of the cruisers was able to take any satisfactory measurements on the 3750-meter wave.

In some of the curves it is seen that the observations are exceedingly irregular, the day signals showing as much variation as the night signals during the July tests. In addition to the observations shown on the curves, faint day signals from the *Birmingham* were received at Brant Rock at a distance of 1325 miles, and again at 1720 miles, while the Brant Rock short wave was received faintly on the *Birmingham* at 1325 miles. All of these observations are beyond the range of calculated day audibility and show that there was an abnormally low absorption on these days.

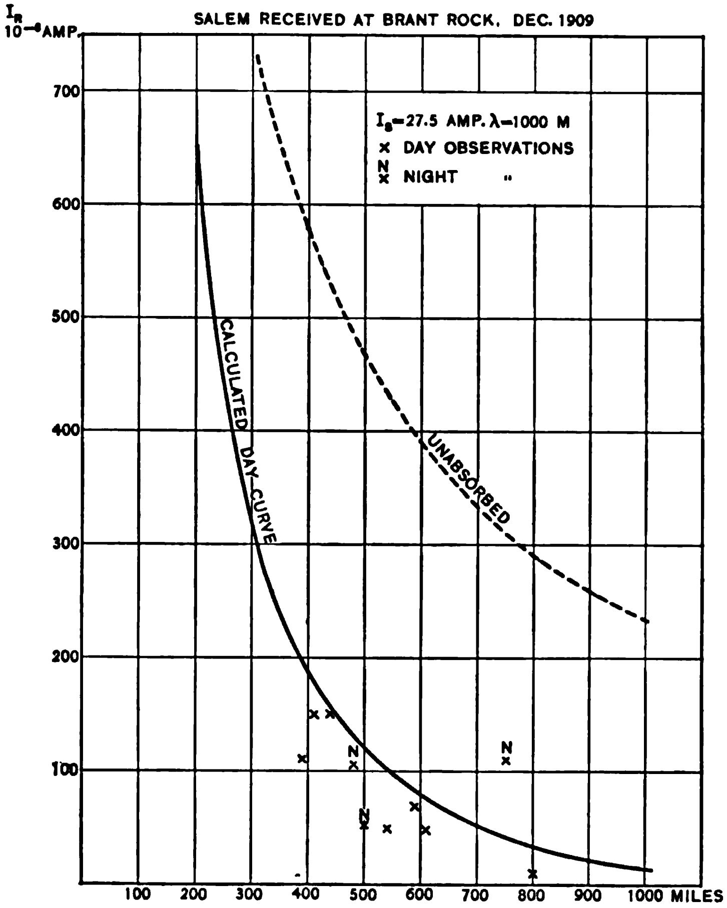

Fig. 15

Night signals during this voyage were also heard at times at great distances, the Brant Rock short wave being received on the

Birmingham at 2550 miles, while on the same night both waves from the *Birmingham* were received at Brant Rock.

MAY EXPERIMENTS

During the month of May the *Birmingham* returned from Liberia to Hampton Roads, and the results of the telephone observations taken during this voyage are shown in figures 24 to 27.

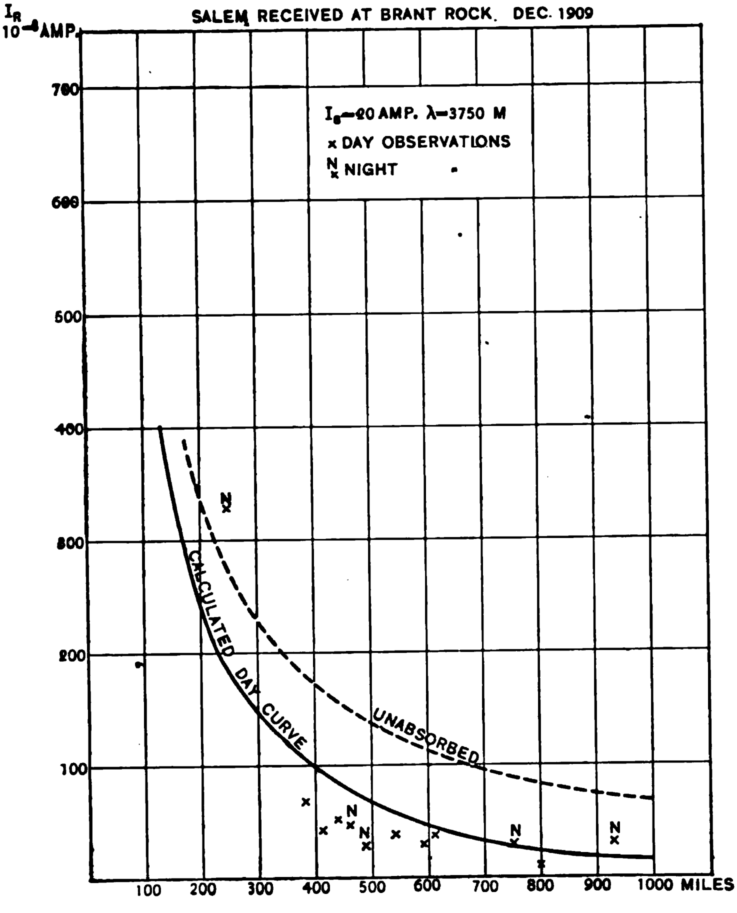

Fig. 16

Within the range covered by the curves the day observations are not as irregular as during the March voyage, although, as was also the case in March, some of the night observations lie above the curve calculated for zero absorption. As has already been said in describing the July experiments, these may be due to errors of observation, or possibly to some kind of reflection from the upper atmosphere.[16] Beyond the range of the curves abnormal signals were again observed, faint day signals of the Brant Rock long wave being received on the *Birmingham* at 2330 miles,

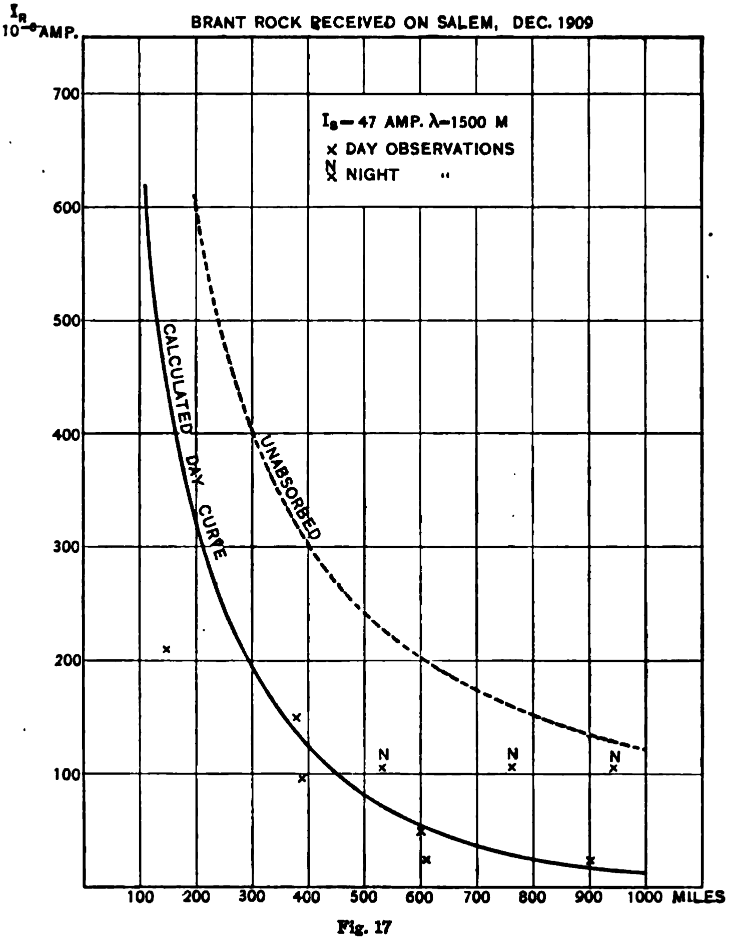

Fig. 17

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[16] There can be no doubt that at times something of the nature of a reflection of signals from the upper atmosphere takes place. During the past winter the Norfolk station sending at a wave length of 1000 meters and with an antenna current of 10 or 12 amperes and antenna height below 200 feet was distinctly heard at night at the Mare Island Navy Yard in San Francisco, a distance of approximately 2000 nautical miles across the continent. Although it is possible that over sea water a clearing up of the atmospheric absorption would have explained this phenomenon, when we take into account the ground absorption which is probably independent of day and night and generally much greater than the atmospheric absorption, this explanation becomes untenable.

and the short wave at 1305 miles. Night signals from Brant Rock were first received at 2776 miles and were heard without interruption from that point on. Both waves from the *Birmingham* were received faintly in the daytime at Brant Rock at 2090 miles, and the long wave again at 1315 miles, no other day signals being received until the distance was reduced to 815 miles. Night signals were received by Brant Rock from the *Birmingham* first at 2418 miles and continued nightly for the rest of the voyage, though very irregular in intensity. This remarkable continuation

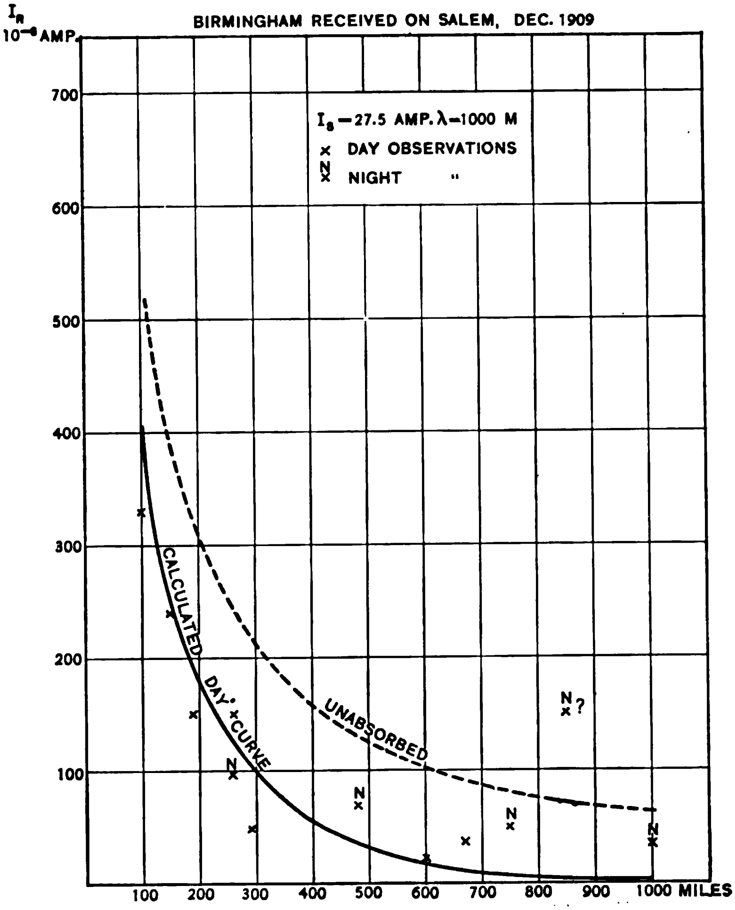

Fig. 18

of long range night communication must be considered exceptional so late in the year, though perhaps it would not be so considered in midwinter.

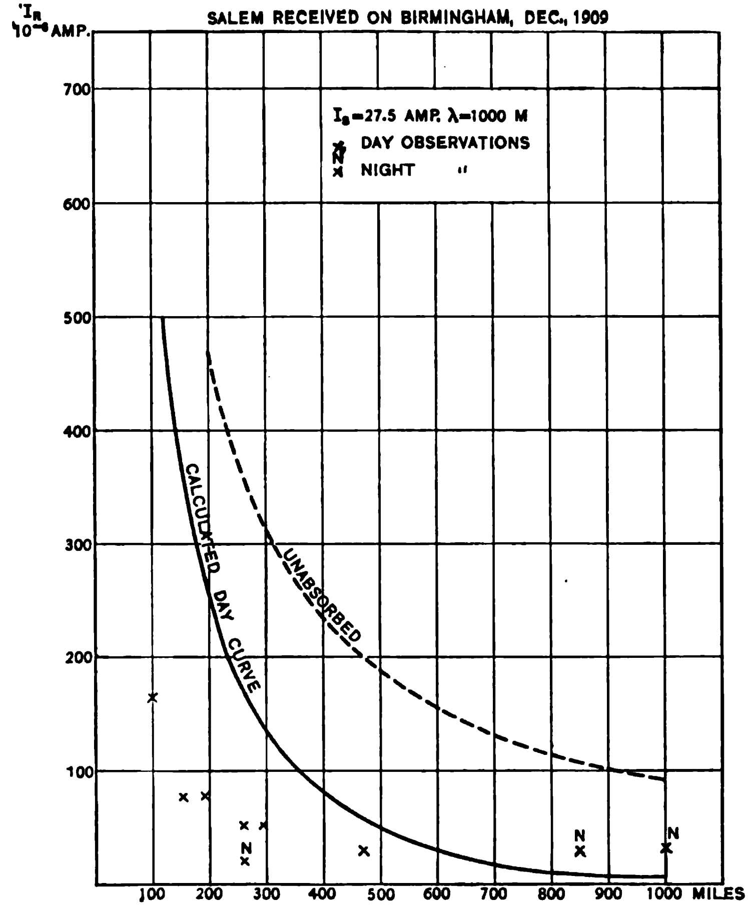

Fig. 19

TORPEDO-BOAT TESTS

In order to test the validity of equation (3) for very short wave lengths and small antennas, the torpedo boats *Stringham* and *Bailey* were detailed to carry out a series of tests in Chesapeake Bay during the month of November, 1910. The two boats were fitted with small 120-cycle directly connected sending sets which, however, could be coupled loosely enough so that but one wave length was radiated. The flat-top antenna of the *Bailey* consisted of four wires 2 feet apart, 80 feet long, 32 feet above the water. The

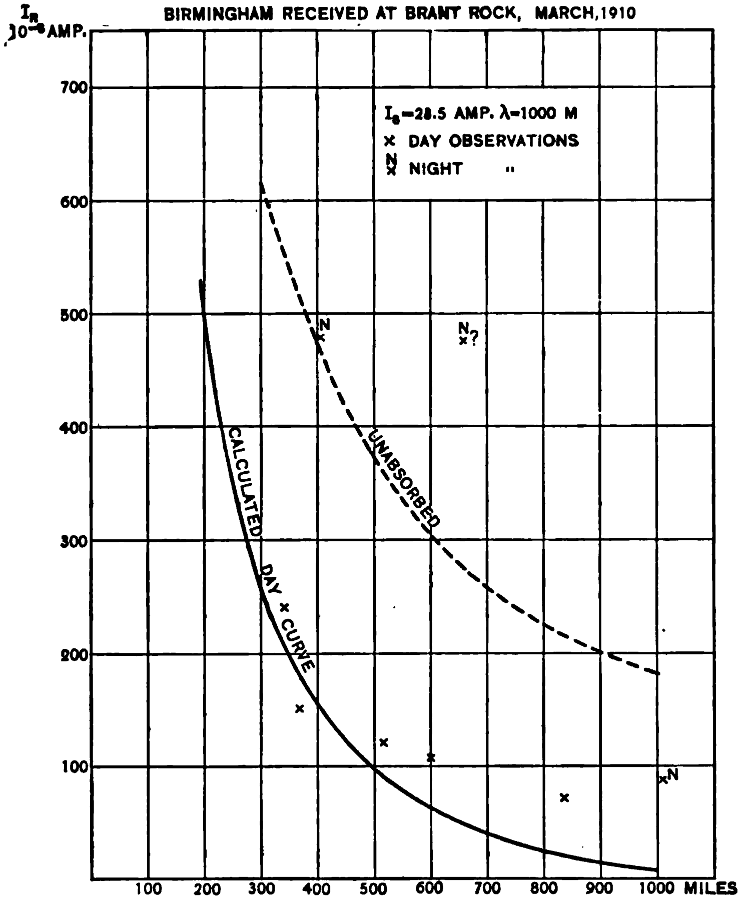

Fig. 20

antenna capacity was 0.000875 microfarad; the closed circuit condenser consisted of Leyden jars in air having a capacity of 0.015 microfarad. The length of the wave radiated by the *Bailey* was 280 meters.

The antenna of the *Stringham* consisted of four wires 2 feet apart, 135 feet long, and 48.5 feet above the water. Its capacity was 0.00134 microfarad. The closed circuit condenser was the same as that of the *Bailey*. The length of the *Stringham's* radiated wave was 340 meters. The receiving apparatus of both boats was of the latest inductively coupled type, and perikon detectors were used which were standardized by comparison with electrolytic detectors, which experiments have shown to have a constant sensitiveness when properly adjusted. The ratio of current sensitiveness of the electrolytic to the perikon in both cases was approxi-

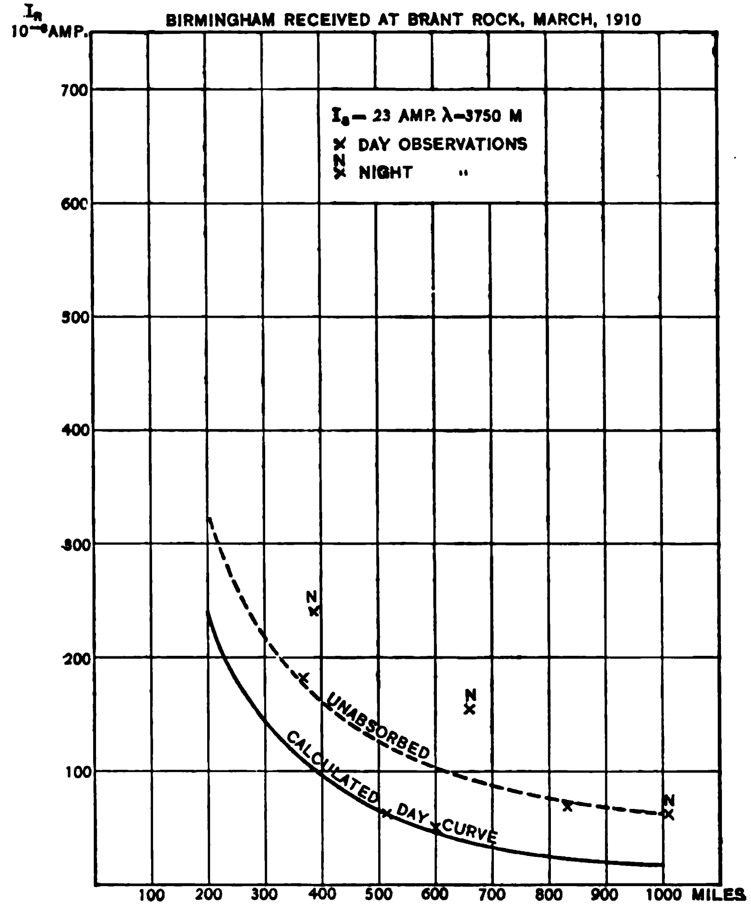

Fig. 21

TABLE XVII

	Distance, Nautical Miles	Stringham Received on Bailey $\lambda = 340$ m			Bailey Received on Stringham $\lambda = 280$ m			I_R Average of Received Currents Corrected to Electrolytic and to $I_S = 7.2$ amp. 10^{-6} amp.
		I_S amp.	Received Current 10^{-6} amp.		I_S amp.	Received Current 10^{-6} amp.		
			Observed	Corrected to $I_S = 7.2$ amp.		Observed	Corrected to $I_S = 7.2$ amp.	
Nov. 3, 1910	21.5	5.45	170	225	5.4	....	....	253
	33	6.00	132	159	5.1	87	123	158
	43	6.14	68	80	5.1	86	121	112
	55	6.00	58	70	5.1	76	107	99.0
Nov. 7,	65	6.27	55	63	7.5	75	72	75.5
	83	6.54	51	56	7.5	57	55	62.2
	100	6.00	39	47	7.2	45	45	51.6
Nov. 8,	122	6.55	23.9	26	7.0	32	33	33.0
	131	6.27	24.5	28	7.0	33	34	34.8
	156	6.82	Interference		7.0	18	18.6	20.9

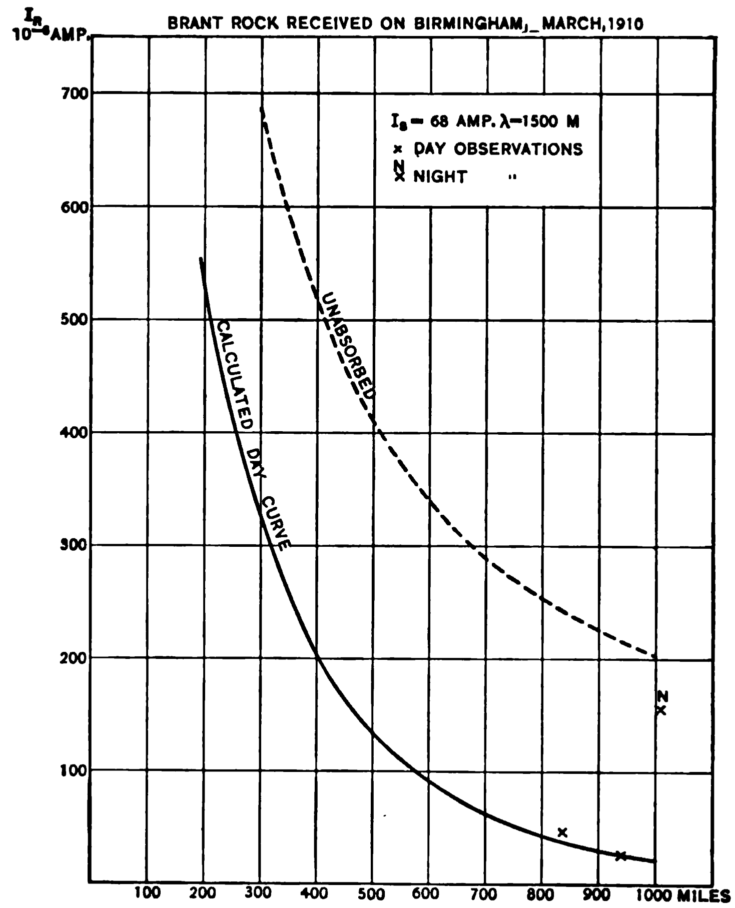

Fig. 22

mately 1.12. The telephones on both boats were of approximately the same sensitiveness and were of 2000 ohms resistance with an inductive resistance under working conditions of about 4000 ohms.

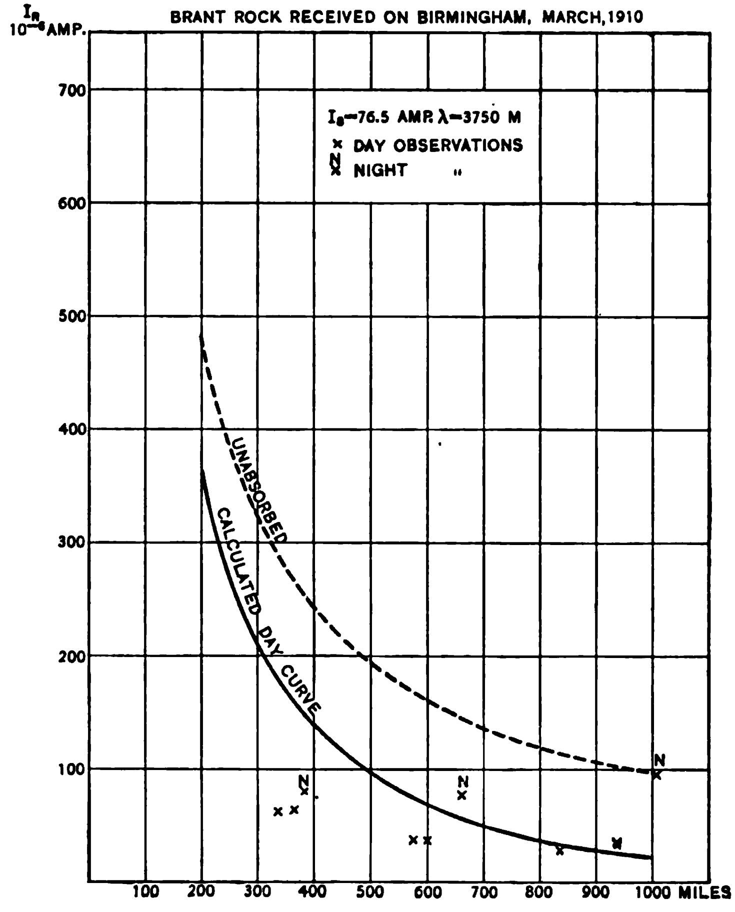

Fig. 23

The observations of these tests, shown in Table XVII, were taken with great care, the engines being stopped during the time of observation. Each one is the mean of a number of readings.

In the last column are given the received currents averaged for both boats corrected to a sending current of 7.2 amperes and to the readings of the electrolytic detector. In Fig. 28 is shown the curve as calculated from Table XVI for antenna heights of 37.5 feet, a sending current of 7.2 amperes, and a wave length of 300 meters. The agreement is remarkable, considering the fact that the table from which the theoretical curve was calculated was based on data derived from ships with 130-foot masts working at

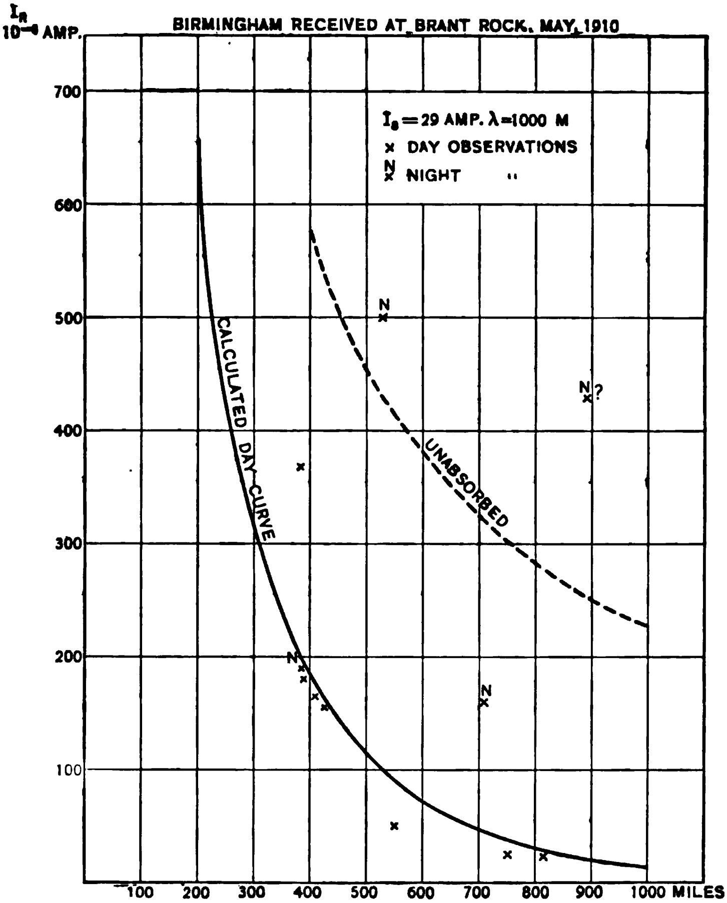

Fig. 24

a wave length of 1000 meters and employing a spark frequency of 1000 per second. These results show, as has often been observed in our laboratory, how little the ratio of sending currents and received signals depends on the spark frequency, the telephones apparently never showing the added sensitiveness for high frequencies exhibited in the case of sinusoidal alternating currents.

SUMMARY AND CONCLUSIONS

Quantitative measurements have been carried out in long distance wireless telegraphy up to 1000 miles for the purpose of determining the law of the variation of strength of signal with distance.

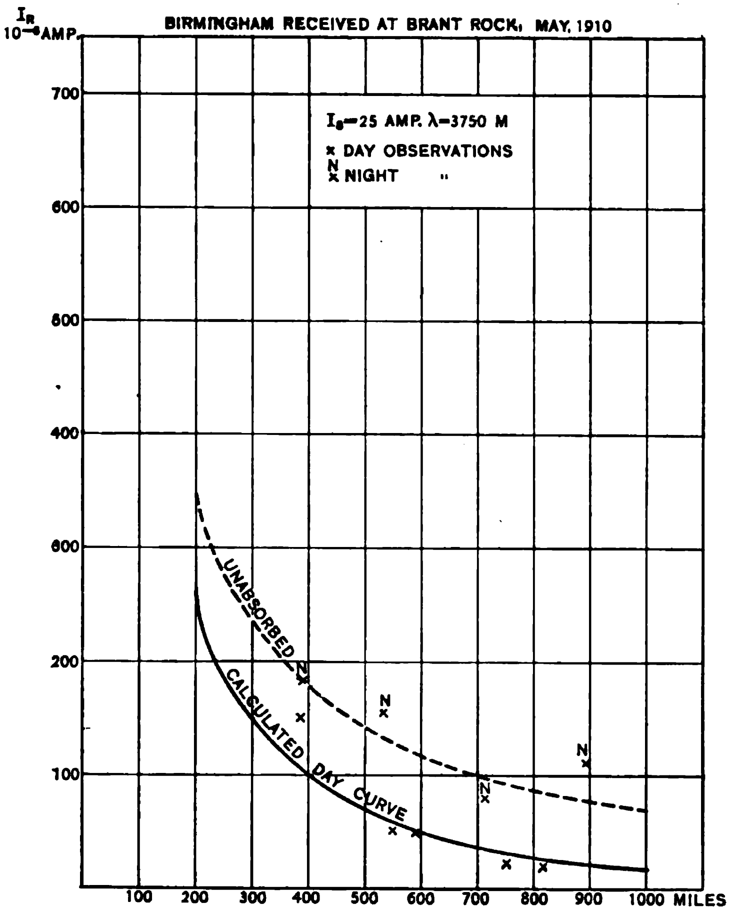

Fig. 25

Supplementary work was also done on the effect of height of antenna and wave length on sending and receiving.

The results are given briefly as follows:

(*a*) Over salt water the electrical waves decrease in intensity in proportion to the distance as found by Duddell and Taylor. In addition they are subject to an absorption which varies with the wave length and which may be expressed mathematically by the term e^{-Ad}.

The complete expression for the received current is then

$$(2) \quad I_R = \frac{K}{d} e^{-Ad}$$

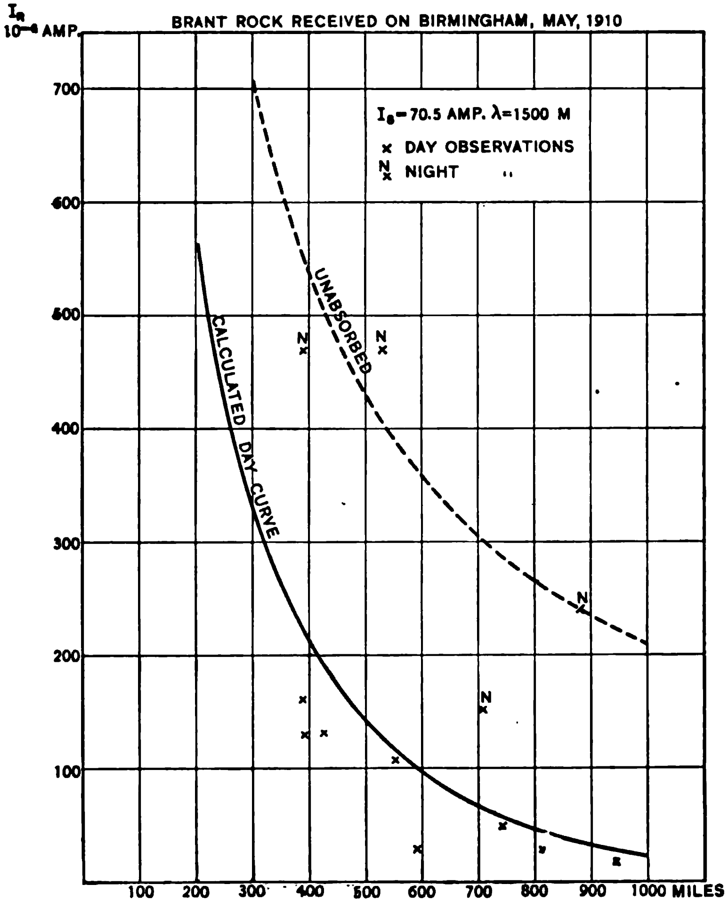

Fig. 26

This is true in general for day transmission. The absorption at night is entirely irregular varying from zero to the day value,[17] but is on an average much less during the winter than in summer.

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[17] The great variations in night absorption make useless all attempts to judge the quality of wireless apparatus from night distances. For this purpose only observations on the average day range have any value.

Variations also appear to occur during the daytime, but these are probably in general small.

(*b*) The received antenna currents between two stations with salt water between are proportional to the product of the heights[18] of the sending and receiving antennas and inversely proportional to the wave length, provided the antenna resistances remain constant. These experiments were carried on with flat-top antenna

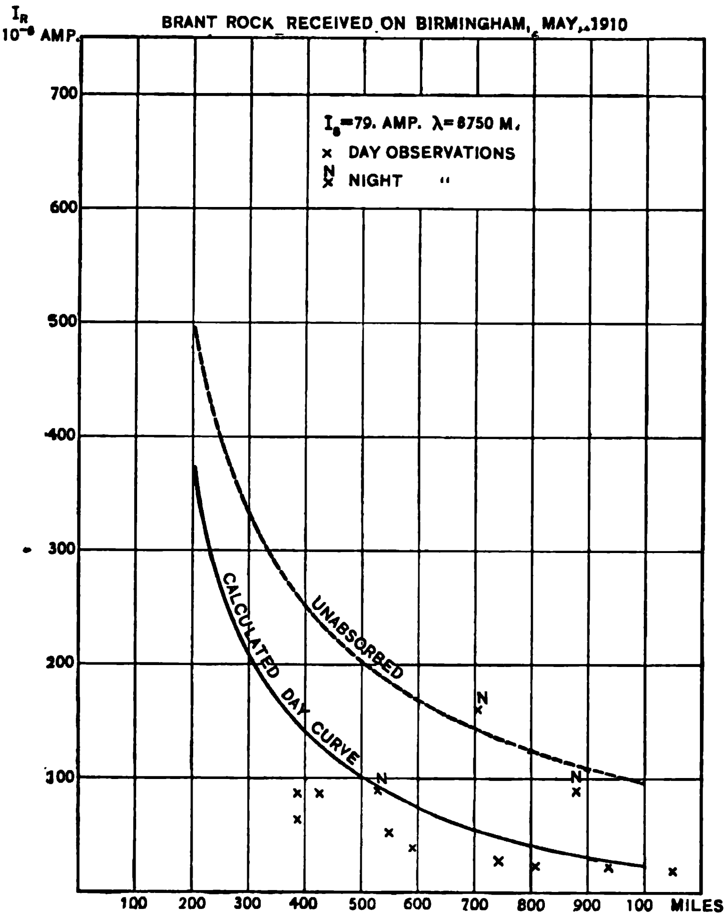

Fig. 27

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[18] The experiments indicate that for the greatest efficiency of a flat-top antenna the vertical lead wires should be bunched so as to reduce their capacity as much as possible and concentrate the capacity at the greatest height.

heights of from 30 to 80 feet and wave lengths from approximately 1500 to 4000 meters.

(*c*) Taking account of the influence of antenna height and wave length equation (2) may be extended and a general day transmission formula written as follows

$$(3) \quad I_R = 4.25 \frac{I_S h_1 h_2}{\lambda d} e^{-\frac{0.0015 d}{\sqrt{\lambda}}}$$

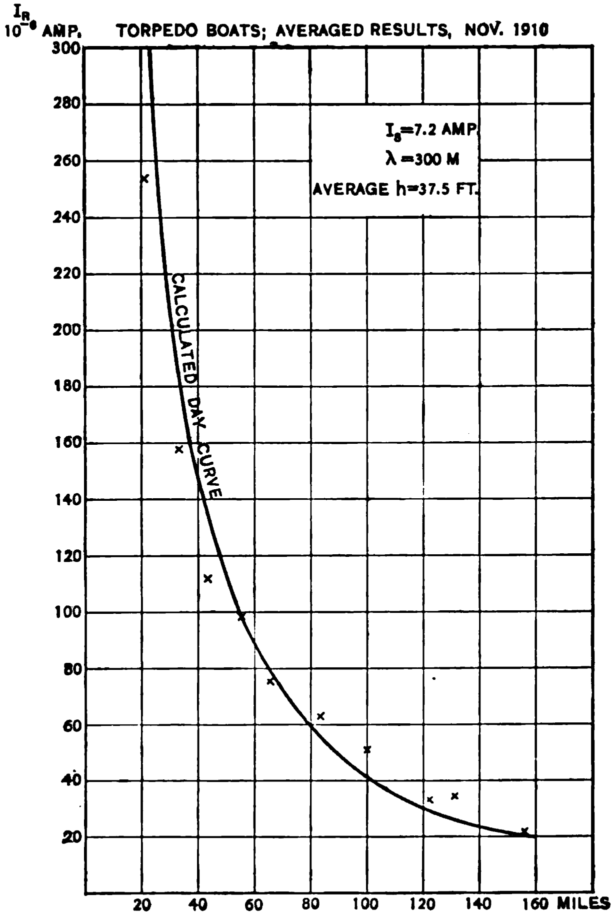

Fig. 28

where the currents are given in amperes and all lengths in kilometers.[19] This formula has been tested for sending currents from

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[19] From this it would appear that it is advisable to rate stations according to the magnitude of the antenna current, or perhaps better, according to the product of the current into the height.

7 to 30 amperes antenna heights 37 to 130 feet, wave lengths from 300 to 3750 meters, and distances up to 1000 nautical miles.

In regard to the value of the day absorption it is only possible to say that the above expression is satisfied within the limits of error of the observations. It is quite possible that when observations are made at distances of 2000 to 3000 miles, the value of the absorption coefficient will have to be corrected by 10 or even 20 per cent, as this amount of error could exist without discovery at the distances covered in these experiments. It is also possible that the square root law relating the absorption with the wave length is only an approximation.

U. S. NAVAL WIRELESS TELEGRAPHIC LABORATORY,
Washington, February 1, 1911.

THE BEHAVIOR OF HIGH-BOILING MINERAL OILS ON HEATING IN THE AIR

By C. E. Waters

HISTORICAL

In a paper published some months ago, Schreiber[1] gives the results obtained when different cylinder and compressor oils were heated in a specially constructed air bath through which a current of air, carbon dioxide, or steam could be passed. The duration of the tests varied from 16 to 24 hours, and the temperature from 200° to 280°. The percentages of asphaltic material in the oil before and after heating were determined. The results showed that the amount of such material insoluble in benzine and in alcohol-ether greatly increased in the presence of air and of carbon dioxide, but was practically unchanged when the oil was heated in steam. Some of the oils became greatly thickened or covered with a gummy surface skin, while others withstood the test remarkably well, thus demonstrating their fitness for use in steam cylinders. A problem of a similar nature having been submitted to this Bureau, the present writer adopted, without knowledge of Schreiber's work, a method similar to his, but differing sufficiently from it in its details that the publication of this paper seems justifiable, especially as the oils to be tested were intended for use in gas engines. Without going immediately into details, it may be said that both Schreiber and the author heated the oils to a considerably higher temperature than that adopted by most of the previous workers.

A summary of the more important work done along this line may not be out of place.

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[1] Zs. angew. Chem., **28**, pp. 99–103; 1910.

In 1884, Fox[2] investigated lubricating oils by a modification of a method described shortly before by Livache[3] for the recognition of drying oils. The oils were heated in sealed tubes with precipitated lead and the amount of oxygen absorbed was measured.

Zaloziecki[4] passed air through heated mineral oils and found acetic acid in the water formed by oxidation. The distillate had the odor of other members of the series of fatty acids. Engler and Bock,[5] in addition to naphthenic acids, observed the formation of butyric and other fatty acids by blowing air through hot, neutral petroleum.

Charitschkow[6] obtained two series of acid oxidation products, one from the alkali sludge, the other by oxidizing petroleum by air in the presence of alkali at 150°. The latter series he called later[7] "polynaphthene," or "asphaltogenic" acids.

In spite of conflicting statements,[8] it is well established that mineral oils oxidize when raised to moderately elevated temperatures in the air. They may oxidize even at ordinary temperatures when exposed to sunlight, especially in the presence of alkalies. The writer has discussed this subject in another paper, in which it is shown that water and carbon dioxide are formed, in addition to acids that remain in the oil.[9]

Another phenomenon closely connected with the formation of acids is the production of resinous or asphaltic substances when oils are heated in the air. This and the cracking of the oils are both probably concerned in the "carbonization" of gas-engine cylinder oils. The cracking of mineral oils has, of course, been known for several decades, but a knowledge of the other chemical changes mentioned is not so widespread, although no argument is needed to convince one of its importance, especially to users of gas engines.

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[2] Zs. anal. Chem., **23**, p. 434, 1884.

[3] Mon. Sci., [3], **13**, p. 299; Zs. anal. Chem., **23**, p. 262, 1884.

[4] Zs. angew. Chem., pp. 416–419, 1891.

[5] Cf. Chem.-Ztg., **16**, p. 592, 1892.

[6] Petroleum, **2**, p. 480, 1907; J. Soc. Chem. Ind., **26**, p. 402, 1907.

[7] Chem.-Ztg., **33**, p. 1165, 1909.

[8] Hirsch: Chem.-Ztg., **19**, p. 41, 1895.

[9] This Bulletin, **7**, p. 227.

In 1894 Holde[10] determined the asphalt content of certain dark-colored mineral lubricating oils before and after heating to 100° for 10 hours. He found that oils with little or no asphalt originally remained liquid; those with 1.3 to 2.3 per cent became thick and sticky; those with 5 to 6 per cent were changed to a thick resin-like mass. He showed later[11] that the gumming is due not only to a concentration of the asphalt as the oil evaporates, but also to a partial oxidation of the oil.

Adiasiewitsch[12] described the preparation of resinous products by blowing "deoxygenated air" through the residue in the petroleum still, the temperature varying from 150° to 200°. The resultant "resins" varied from thick liquids to solid, asphalt-like masses, and all were soluble in petroleum distillates.

Mabery and Byerley[13] also made asphalt from heavy petroleum residues by blowing air through the mass for four or five days, the temperature being kept at 650° F. Culmer[14] obtained similar results in 40 hours at 193°.

In this connection may be mentioned the belief of Meyerheim[15] that the increase in the asphalt content with time is due to a polymerization of the oil or to a change of the asphalt from its original colloid state to the insoluble form. Radium emanation caused no increase in the amount.

Richardson[16] and Hanson studied the change in viscosity of oils heated in thin layers at temperatures varying from 100° to 201°. In an atmosphere of superheated steam changes exactly similar to those in air were produced. Worrall and Southcombe,[17] however, state that in cylinders heated as high as 750° F. steam causes no chemical change in the oil. The horny or granular deposit at times found in cylinders is Fe_2O_3 or Fe_3O_4 cemented together by oil.

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[10] Mitth. kgl. techn. Versuchsanst., **11**, pp. 261–272; J. Soc. Chem. Ind., **13**, p. 668; 1894.

[11] Ibid., **13**, pp. 174–196; 1895.

[12] See abstract in J. Soc. Chem. Ind., **15**, p. 346; 1896.

[13] Amer. Chem. J., **18**, pp. 141–150; 1896.

[14] Rev. Prod. Chim., **2**, p. 356; J. Soc. Chem. Ind., **19**, p. 525; 1900.

[15] Chem.-Ztg., **34**, p. 454; 1910.

[16] J. Soc. Chem. Ind., **24**, pp. 315–319; 1905.

[17] Ibid., **27**, p. 308; 1908.

Kissling[18] determined the "resinification number" of oils. The amount of material precipitated by petroleum ether was determined after the oils had been heated to 125° to 135° for 12 hours on each of fivė successive days. The results showed that less insoluble matter is formed in the better refined oils. The percentages of insoluble formed may vary a great deal more than the iodine and Maumené values. Kissling later[19] published a somewhat modified method, according to which the oil is treated with alcoholic soda, which extracts the "resin" originally present or formed by heating. The "coke-like" matter is thrown out by benzine. The oils are heated to 150° to 250°.

Letschford[20] studied the oxidation of spindle oils when heated to 95° to 98° for 75 hours. The ratio of the product insoluble in petroleum ether to the original oil was called the "acid coefficient."

It is of fundamental importance to have a satisfactory method for determining the asphalt in oils. One method that has been tried is to determine the diminution in volume when the oil is shaken with concentrated sulphuric acid and then allowed to stand. This has been found to be unreliable.[21]

Distilling off the oil by means of superheated steam has also been recommended.[22] But practically the only method used is the precipitation by means of benzine or other light petroleum distillate. This is based on an observation by Bender.[23] It has been found that the amount of insoluble matter precipitated depends on the boiling-point limits of the benzine used. Hence the necessity for a carefully specified "normal" benzine.[24] Still later, Kissling[25] showed that benzines from different sources, though they may boil between the same limits, are not to be used indiscriminately if the results obtained by different chemists are to be compared. Thus, a sample of Kahlbaum's "normal benzine" gave lower values than benzine from Pennsylvania petroleum. Benzine from an Indian petroleum gave higher values than either of the preceding.

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[18] Chem.-Ztg., **30**, pp. 932–933; 1906.

[19] Ibid., **31**, p. 328; 1907; **32**, p. 938; 1908.

[20] Seifensiederztg., 1908, No. 2; Zs. angew. Chem., **22**, p. 1066; 1909.

[21] Aisinmann: Dingl. Pol. J., **294**, pp. 65–68; 1894; J. Soc. Chem. Ind., **14**, p. 282. Charitschkow: Petroleum, **2**, pp. 99–101; 1906; J. Soc. Chem. Ind., **25**, p. 1140; 1906.

[22] Lecocq: Bull. Soc. Chim. Belg., **22**, pp. 81–87; Chem. Abstr., **2**, p. 1880; 1908.

[23] Mitth. kgl. techn. Versuchsanst., 1890, 311–316; J. Soc. Chem. Ind., **10**, p. 354; 1891.

[24] Holde: Mitth. kgl. Materialprüfungsamt, **27**, p. 143; 1909.

[25] Chem.-Ztg., **33**, p. 1203; 1909.

EXPERIMENTAL

The four oils submitted to this Bureau had the following constants:

Sample	1	2	3	4
Flash point	140°	224°	142°	142°
Engler no. at 50°	3.3	3.4	3.6	2.9
Engler no. at 100°	1.4	1.4	1.5	1.4
Acidity (per cent oleic acid)	0.033	0.024	0.023	0.025
Fatty oil	None.	None.	None.	None.

In the preliminary experiments two mineral oils that had been on hand for a considerable time were used to test the method. Ten-gram samples were heated one at a time in matched Erlenmeyer flasks of 150-cc capacity. The flasks rested on a small tripod of glass rod on the bottom of a large iron crucible, which was covered with a brass plate having a large hole through which the upper two-fifths of the flask projected. The bath was kept at 250° for one and one-half hours, and at the same time a fairly rapid current of air was passed in through a tube of Jena combustion glass bent at right angles at one end. Near the bend was a closely fitting sheath of brass tubing, under which was a fishtail burner for preheating the air. Concordant results could not be obtained on account of the impossibility of accurately regulating the two flames and air current, all three varying from time to time during the day.

A cubical air bath of sheet copper was then constructed. Openings were cut in the movable cover so that four flasks could be suspended by their necks. The sides and top of the bath were covered with sheet asbestos. A "rose" top was used on the burner, and the heating further equalized by means of a circular sheet of brass, resting on a glass tripod about 2 cm high, on the bottom of the bath. The temperature was kept constant within 2° or 3° by means of a thermoregulator. There was nothing to prevent perfect freedom of diffusion of oil vapors and air at the mouths of the flasks.

Four 10-gram samples of the two trial oils were heated to 250° for three hours. The losses by evaporation did not agree very closely. To determine the amount of material insoluble in petroleum ether, 50 cc of the solvent were placed in each flask, which was then corked, shaken gently, and let stand overnight. The insoluble matter, except the coating on the walls of the flasks, was then filtered off in Gooch crucibles containing disks of S. & S. No. 589, Blue Ribbon filter paper, covered with a thick felt of fine asbestos. The results are given in the table:

Sample	A	A	A	A	B	B	B	B
Flask	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
Per cent evaporation	5.00	4.50	6.20	7.90	9.44	7.35	9.29	15.92
Per cent insoluble filtered off.	0.55	0.48	0.51	0.55	0.34	0.42	0.40	0.37
Per cent insoluble in flask	0.10	0.25	0.15	0.05	0.09	0.37	0.39	0.08
Total insoluble	0.65	0.73	0.66	0.60	0.43	0.79	0.79	0.45

Duplicate tests were then made with the four samples of oil submitted to us for examination. The results follow:

Sample	1	1	2	2	3	3	4	4
Flask	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
Per cent evaporation	9.90	9.40	10.75	14.45	7.60	6.50	13.35	16.10
Per cent insoluble filtered off.	0.87	0.91	0.40	0.47	0.08	0.12	0.84	0.60
Per cent insoluble in flask	0.30	1.25	1.40	0.70	0.10	0.20	0.85	0.40
Total insoluble	1.17	2.16	1.80	1.17	0.18	0.32	1.69	1.00

An inspection of the results will show that the chief cause of the irregularities, when duplicates are run, is the insoluble matter remaining in the flask. This is a dark brown, varnish-like coating which does not dissolve in petroleum ether. Even when heated on the steam bath for two or three days with chromic acid mixture, only part of it is removed, but soaking with alcoholic soda for two or three hours so loosens it that it may be rinsed out easily.

Duplicate determinations of the amount of flocculent insoluble matter filtered off agree very well, except the results on No. 4.

The flasks were not placed in the bath in any regular order, but in three of the heatings flasks (*a*) and (*d*) gave low results on the coating or "varnish" (oils A, B, 1, and 2). This does not hold for oils 3 and 4, but even here flask (*a*) showed less varnish than (*b*) and flask (*d*) less than (*c*).

It may be mentioned parenthetically that oil No. 3 was recommended by us as the best of the four. We have since learned that one of the other oils was first given a trial by the company for which the test was made. It proved to be entirely unsuitable, while No. 3, which was then used, has been satisfactory.

Variations in the condition of the walls of the flasks, all of which had been used for other purposes, seemed to be a possible explanation of the discrepancies in the amounts of "varnish" found. Accordingly, four new Jena flasks were carefully cleaned and used to obtain the following results. Only oil B was used.

Flask	(a′)	(b′)	(c′)	(d′)
Per cent evaporation	21.55	22.60	23.15	25.40
Per cent insoluble filtered off	0.32	0.32	0.44	0.61
Per cent insoluble in flask	0.17	0.08	0.50	0.92
Total insoluble	0.49	0.40	0.94	1.53

A series of results was also obtained with a new set of flasks of "resistance" glass. Oil B was again used.

Flask	(a″)	(b″)	(c″)	(d″)
Per cent evaporation	10.35	11.55	15.80	16.45
Per cent insoluble filtered off	0.33	0.44	0.25	0.23
Per cent insoluble in flask	0.45	0.82	0.29	0.11
Total insoluble	0.78	1.26	0.54	0.34

A consideration of all the figures obtained with oil B shows that while the "insoluble filtered off" varies from 0.23 to 0.61 per cent, nine of the twelve results lie within the limits 0.32 and 0.44 per cent. The average of these is 0.37 per cent, and the average for all twelve is 0.37¼ per cent.

Flask	A	B	C	D
Per cent varnish, first heat	0.11	0.30	1.20	0.48
Increase in varnish, second heat	0.82	1.94	1.03	0.46
Per cent insoluble, first heat	0.26	0.30	0.55	0.32
Per cent insoluble, second heat	0.50	0.40	0.57	0.64

Another interesting series of results was obtained by heating two lots of oil B in the resistance glass flasks. For the second heating, the varnish was not removed, the flasks being thoroughly washed out with petroleum ether before a new lot of oil was introduced.

At the second heating the amounts of both varnish and insoluble are greater than at the first, except in one instance.

It is unfortunate that Schreiber does not publish any duplicate determinations on the same oil, nor is he able, with his apparatus, to make any distinction between the "varnish" and the flocculent, insoluble matter. His statement that the formation of "asphalt" depends on oxidation we can fully confirm, for in some of the earliest experiments we heated the oil in glass-stoppered bottles and found only traces of insoluble matter and no varnish at all.

In order to further test the possibility of variations being caused by the nature of the walls of the containing vessels, glass tubes of 20 mm bore and 10.5 cm long were made. Tubes of the same inside dimensions were made of ordinary brass, cold-rolled steel, and also from a steel containing 0.8 per cent carbon, a vanadium steel, a chrome-vanadium steel, and cast iron. These tubes were made in pairs. One of the vanadium steel tubes leaked so badly that it could not be used. Both of the cast-iron tubes had fine pores through which a little oil escaped, but they became plugged up at the first heating. All of these tubes, except those of cold-rolled steel and brass, were made from the centers of the billets from which the standard samples issued from this Bureau were cut. Their size was necessarily limited and this had the disadvantage that only 5 grams of oil could be heated at a time, for when 25 cc of ligroin were added after heating there was just enough space left to insert a cork safely. The metal tubes were made with flaring, knife-edge rims to diminish creeping of the oil when the insoluble was filtered off.

In every case the oil, after dilution with petroleum ether, was allowed to stand about 22 hours, it having been found that the precipitate was less apt to clog the filter than when a shorter time elapsed.

For the heatings in the different tubes three oils, designated as B, C, and D, were used. They had been kept for a long time in closed tin cans. The organic acidity, saponification number, and flash point were determined.

Sample	B	C	D
Organic acidity (as per cent oleic acid)	0.08	0.03	0.07
Fatty oil (approximate)	None	None	0.5
Flash point	205°	195°	195°

Oil B gave an incipient flash at 185°. The Pensky-Martens closed cup flash-point apparatus was used.

A complete series of heatings was run only with oil B, this having been considered unnecessary with C and D. The results are given below, expressed as percentages of insoluble matter and varnish.

GLASS TUBES

Oil	B	B	B	B	C	C	D	D
Varnish	0.44	0.03	0.08	0.10	0.11	0.09	0.04	0.04
Insoluble	0.10	0.07	0.08	0.05	0.10	0.08	0.07	0.09

BRASS TUBES

Oil	B	B	B	B	C	C	D	D
Varnish	......	......	......	......	0.02	0.03	......	......
Insoluble	0.15	0.18	0.15	0.16	0.13	0.15	0.07	0.06

CAST-IRON TUBES

Oil	B	B	C	C	D	D
Varnish	0.07	0.01	Trace	Trace	Trace	Trace
Insoluble	0.06	0.06	0.08	0.08	0.07	0.05

CHROME-VANADIUM STEEL TUBES

Oil	B	B	B	B	C	C
Varnish	0.05	0.04	0.03	0.02	Trace	0.01
Insoluble	0.07	0.06	0.08	0.08	0.14	0.13

In the remaining tubes only oil B was heated.

Tube	Vanadium steel		Cold-rolled steel				0.8 carbon steel			
Varnish	0.02	0.04	0.04	0.03	0.02	Trace	0.03	0.02	0.03	0.03
Insoluble	0.07	0.08	0.08	0.08	0.09	0.09	0.07	0.10	0.07	0.07

The above results seem to show that the material of which the tubes are made exerts an influence upon the amount both of the varnish and the precipitate formed in the oil itself. The differences are not great, but neither are the actual amounts large, most likely because of the relatively small surface of oil exposed to the action of the air. This area was only 3.14 sq cm, while only double the amount of oil in a flask exposed a surface about nine times as great. The most striking discrepancy in the results is that oil D yielded less insoluble in the brass tubes than in those of glass, while B and C gave much larger amounts in the brass tubes. The reason for this may be that D contained about 0.5 per cent of fatty oil, the others being straight mineral oils.

That the three oils show wider differences when heated in flasks is shown by the following figures obtained with resistance glass flasks. The percentages of evaporation, varnish and insoluble are given.

Oil	B	B	B	B	C	C	C	C	D	D	D	D
Flask	(a)	(b)	(c)	(d)	(a)	(b′)	(c)	(d)	(a)	(b′)	(c)	(d)
Evaporation	19.00	19.03	19.95	15.08	17.15	25.75	13.05	15.77	23.93	22.83	13.42	19.32
Varnish	0.18	0.74	0.75	0.25	0.37	1.14	0.38	0.43	1.01	0.57	1.27	1.25
Insoluble	0.28	0.48	0.40	0.29	1.90	2.29	1.88	1.81	2.30	1.89	2.25	2.50

Flask (b′), first used for oil C and subsequently for D, replaced (b) in which B was heated. It is curious that for one oil it gave high and for the other low results.

In our opinion the formation of "asphalt," or as we have called it, "insoluble," is due to partial oxidation of the oil rather than to polymerization or to concentration of the asphalt as the oil evaporates. As mentioned above, there was practically no formation of insoluble when the oil was heated to 200° for three hours in stoppered bottles. When heated for the same length of time in flasks loosely covered with watch-glasses, there was opportunity for atmospheric oxygen to enter as rapidly as it was absorbed by the oil. At the same time the lack of perfect freedom of diffusion allowed the escape of only the more volatile constituents so that the change in weight was negligible. No varnish was formed, but the following percentages of insoluble were obtained: 0.47, 0.52, 0.38, and 0.33. Not enough of this oil was available for a test in the apparatus finally adopted.

Although the figures obtained by heating duplicate samples of the same oil side by side are often less concordant than could be desired, yet on the whole the method seems to be capable of yielding data of value; this in spite of differences caused by unequal heating, variations in the rate of interdiffusion of oil vapors and air and, apparently, obscure catalytic phenomena influenced by the nature of the material in which the oil is heated. At present the method can be used to compare a limited number of oils with one another. To make it of perfectly general application would require a standard apparatus of carefully specified dimensions and material. The petroleum ether used would also need to be of very definite composition. Observing these and other obvious precautions, the requirements of the case would be more than met, for in actual practice the conditions must vary considerably more than in a laboratory experiment.

It is not claimed by anyone who has worked along this line that the method does more than indicate what may be expected to happen when an oil is in actual use, or rather, which of two or more oils will behave least badly. But even a slight indication is of greater value than complete ignorance, and a laboratory test is more rational than placing implicit confidence in a dealer's statements.

It is our intention to go more fully into the question of standardization and also to study the effect of the addition of fatty oils and other substances to the mineral oils before heating.

WASHINGTON, December 14, 1910.

THE DETERMINATION OF VANADIUM IN VANADIUM AND CHROME-VANADIUM STEELS

By J. R. Cain

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I. INTRODUCTION

Vanadium has been called by metallurgists a "homeopathic" remedy because of the remarkable results obtained by small additions of it to other metals, notably to steel. Carbon steels or alloy steels as produced in this country when they carry vanadium usually contain from 0.10 per cent to 1.00 per cent. It has been claimed by some that the element acts by removing dissolved gases, especially nitrogen, from the molten steel, with resulting elimination in the slag of the greater part added, and that the amount left in the steel itself is of secondary importance. However, others have shown that the microscopic structure of steel is greatly modified by the residual vanadium in the amounts in question here, and, as might be expected, there are corresponding changes in physical properties. Hence it will be seen that a high degree of accuracy in determining vanadium in steel is to be desired. Considerations such as these, combined with requests from many sources, led the Bureau of Standards to undertake the preparation of a vanadium standard steel similar to the analyzed plain carbon steels which it has issued for some time. In conformity with the usual practice of the bureau, samples were analyzed by its chemists and by prominent technical and works chemists (eleven in all). The first figures thus obtained for vanadium were so unexpectedly discordant as to indicate sources of error in methods used which had probably been overlooked or unrecognized. Accordingly, some of the most probable of these were investigated by the bureau. The results of this investigation were communicated to those participating in the cooperative work and a satisfactory concordance in the final vanadium figures was very soon obtained. Inasmuch as some of these sources of error do not seem to have been sufficiently emphasized in the literature, concise statements regarding them may be of service. Three classes of methods were used by the cooperating analysts:

1. CLASS A

Methods like that first described by Campagne[1] and found with little variation from the original in many textbooks on steel analysis. The hydrochloric acid (ferric) solution of the steel is extracted with ether, which removes most of the iron, leaving the vanadium in the aqueous layer. This portion is evaporated to dryness and the operation repeated two or three times with fresh portions of hydrochloric acid. The latter reduces the vanadium to the quadrivalent state; the final evaporation is made with sulphuric acid and is continued until fumes are given off strongly. The solution is then titrated against permanganate.

2. CLASS B

Methods depending upon the reduction of quinquivalent to quadrivalent vanadium by ferrous sulphate, either by titrating directly against a ferrous solution or adding excess of the same and titrating back with bichromate; potassium ferricyanide is used either as an external indicator or by adding it directly to the solution undergoing titration.

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[1] Ber., **36**, p. 3164; 1903.

3. CLASS C

Most of the iron is extracted as under class A, the hydrochloric acid replaced by nitric acid and the vanadium separated from iron, chromium, etc., by pouring into a boiling solution of sodium hydroxide. The vanadium goes into the filtrate, and is precipitated by mercurous or lead salts, the final estimation being either gravimetric or volumetric.

It seems likely that these three classes of methods comprise those most used in this country, inasmuch as the group of cooperating chemists was typical. The same methods are used with little or no change for the analysis of chrome-vanadium steels carrying usually from 0.2 per cent to 5 per cent chromium.

II. SOME SOURCES OF ERROR

1. GENERAL ERRORS

An error in all methods where final titration is made against permanganate may arise by failure to deduct the blank caused by the presence of elements other than vanadium; this may be particularly high in such methods as that of Campagne where, if the ether extraction is not carefully done, there may be large amounts of ferric sulphate present during the titration. Campagne himself speaks (loc. cit.) of this point, but it is not usually mentioned in textbooks. If salts yielding green or blue solutions are present, these may obscure the true end point, requiring several tenths of a cubic centimeter of tenth normal permanganate in excess. Indeed, in low vanadium products the blank may be much larger than the amount required by the vanadium, or if the analyst does not make a qualitative test for vanadium he may report its presence when the steel contains none. Another point to be observed is the temperature of the solution being titrated. The optimum temperature is 70° to 80° C.[2] It is almost impossible to secure a good end point in a cold solution. On the other hand, the work of Sarkar and Dutta[3] and of others on the reduction of permanganate by hot sulphuric-acid solutions of manganous sulphate shows the importance of not titrating at too high a temperature.

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[2] Hillebrand: Analysis of Silicate and Carbonate Rocks, Bull. 422, p. 151. U. S. Geol. Survey.

2. ERRORS INCIDENT TO METHODS OF CLASS A

(*a*) *Iron reduced during ether extraction.*—During the ether extraction there is almost always some iron reduced to the ferrous condition; this is not always reoxidized during the course of the analysis before the titration and therefore might be calculated as vanadium if this fact is not taken into consideration.

(*b*) *Action of sulphuric acid on organic substances.*—The ether, or impurities in it, may act on the strong sulphuric acid when the solution is evaporated to small volume with this acid. There are then present substances which may act on permanganate. In this laboratory separation of carbonaceous material has been observed at this stage, with accompanying odor of sulphur dioxide.

(*c*) *Too early addition of sulphuric acid.*—The addition of sulphuric acid before the solution has been repeatedly evaporated with fresh portions of hydrochloric acid is to be avoided, because, if the sulphuric acid is added before reduction of vanadium to the quadrivalent state has been attained, the reduction is likely to be incomplete.

(*d*) *Too prolonged evaporation with sulphuric acid.*—If the evaporation with strong sulphuric acid is too prolonged or carried out at too high a temperature the reverse reaction, resulting in the oxidation of vanadium tetroxide to vanadium pentoxide by the sulphur trioxide, may take place.[4]

(*e*) *Presence of other metals.*—No other metals capable of oxidation to higher valence by permanganate should be present. Those most likely to be encountered in steel analysis are chromium, molybdenum, and tungsten. The latter two may be removed before titration without great difficulty; the methods hitherto given for separating vanadium and chromium are so laborious that this precaution is often omitted in the case of chromium. A correction for the latter is invariably necessary, particularly in some steels where the chromium and vanadium may be present in the ratio of twenty or forty to one. Moreover, the amount of chromium oxidized to chromic acid is greater when titration is made at 70° to 80°, as is imperative for a good vanadium end point than where the solution is titrated cold, as is sometimes recommended. (For details regarding this correction for chromium, see "Analysis of Silicate and Carbonate Rocks," Hillebrand, Bull. 422, pp. 152–154, U. S. Geol. Survey.)

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[3] Zs. Anorg. Chem., **67**, p. 225; 1910.

[4] Koppel and Behrendt: Zts. Anorg. Chem., **35**, p. 156; 1903.

3. ERRORS INCIDENT TO METHODS OF CLASS B

Methods requiring the use of ferricyanide as indicator for ferrous salts when quadrivalent vanadium and ferrous salts are also present, must of necessity be very uncertain, yet these are the conditions under which the determination is carried out. The reason for this is very evident, when it is remembered that ferricyanide in acid solution rapidly oxidizes quadrivalent vanadium to the quinquivalent condition with resulting production of ferrocyanide. The latter reacts at once with the ferric iron, so that a blue color is present in the drops of indicator as soon as an appreciable amount of vanadium is reduced and long before the color due to excess of the titrating solution makes its appearance. Consequently such methods, if at all applicable, must yield results varying with the operator and requiring arbitrary and uncertain correction factors. Much difficulty was experienced in attempting to determine vanadium in pure vanadium solutions by this method; the reason for this, as stated above, was soon discovered, and later references to the same matter were found in the literature.[5]

4. ERRORS INCIDENT TO METHODS OF CLASS C

Vanadium is almost always carried down by the precipitate of ferric and chromic hydroxides, etc., upon pouring into sodium hydroxide. Usually two or three precipitations are necessary to obtain all the vanadium in the alkaline filtrate. The difficulty seems to be largely due to the presence of manganese, which, of course, the ether does not extract, for by working in the absence of manganese it has been found possible to make good separations with one precipitation. However, there is no simple method for removing manganese at this stage of a vanadium determination in steel without introducing other complications. If chromium is present another difficulty is added, for part of the manganese is oxidized by the air and precipitated while the sodium hydroxide solution is being boiled to secure complete precipitation of chromium and complete extraction of vanadium from the precipitated hydroxides; this peroxide rapidly oxidizes some of the chromium to chromate, which goes into the filtrate with the vanadium. If the sodium hydroxide precipitation is repeated, or a third precipitation is necessary, as may happen, a very large amount of chromium goes into the filtrate. In fact, the first operation leaves enough chromium with the vanadium to introduce serious error in determining the latter unless a correction is made; furthermore, the same cause may require appreciable correction to be applied to the chromium. The addition of sulphurous acid to the acid solution of the steel just before it is poured into the alkali, as is recommended sometimes, does not help, for, of course, it is not effective after the solution is strongly alkaline. Another source of trouble is the organic matter mentioned above as sometimes coming from ether; this causes appreciable amounts of iron and chromium to dissolve in the filtrate with the vanadium. It is evident that all of the sources of difficulty, except the last mentioned, are present in even greater degree when an attempt is made to carry out the caustic soda separation without a preliminary extraction of most of the iron by ether. Thus it will be seen that to separate the vanadium from the iron and to obtain all of it in the filtrate may be, and usually is, a long and complicated operation. When this is accomplished there may be present a large amount of chromium, and this occasions another series of difficulties, for the chromate precipitates with the vanadate, whatever the method of precipitation. The only alternative is to titrate the vanadium in presence of the chromium, making the uncertain corrections above mentioned, or to make an electrolytic separation as described later.

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[5] Campagne, loc cit. Brearley and Ibbotson: Analysis of Steel Works' Materials, p. 89.

When attempt is made to extract vanadium from steel by fusion of the oxides obtained by evaporating and baking a nitric acid solution of the metal, an old method which is now probably little used for this class of material, the same series of difficulties as enumerated under class C is encountered. It seems almost impracticable to extract quantitatively, say, one-tenth of 1 per cent of vanadium in this manner without undue expenditure of time and labor.

It is clear, then, that there are marked defects in the most commonly used methods for determining vanadium in steel, unless the analysis is conducted with extreme care, requiring more time than is usually available in a technical laboratory, or unless the analyst is so experienced that he can recognize and correct for disturbing factors. Accordingly, the present research was started with the hope that a simpler and more accurate procedure might be outlined, and one which would at the same time be reasonably short.

III. PRELIMINARY WORK TOWARD A NEW METHOD FOR VANADIUM

Much work was done with the idea of determining vanadium without a preliminary separation from iron. It seemed possible that the vanadium might be oxidized to vanadate and then reduced by hydrobromic acid by distilling in an apparatus suitable for collecting the liberated bromine in alkali. The difficulty, however, is to secure oxidation of the vanadium and then get rid of the excess of oxidizer without at the same time reducing some vanadic acid. It was found that the vanadium of a dilute sulphuric acid solution of a vanadium or chrome-vanadium steel could be oxidized easily enough in the cold by manganese dioxide without converting any noticeable amount of chromium to chromate, the excess of manganese dioxide being eliminated by filtration. But when such a solution was placed in the distilling apparatus and distilled after the addition of a large excess of hydrochloric acid and potassium bromide, as recommended by Edgar,[6] there was almost always more bromine liberated than corresponded to the vanadium present. Many efforts were made to get rid of the disturbance, such as long boiling of the oxidized steel solution before placing in the distilling apparatus, reduction of the amount of suphuric acid used for solution to the minimum necessary, etc., but while the results were usually as accurate as those obtained by any of the methods above described, there were occasional and unexplained irregularities which finally led to the abandonment of the method for technical purposes. This is regrettable, for, theoretically, such a procedure is ideal; practically it would be extremely short and simple. It seems likely that the trouble experienced was due either to the known solubility of manganese dioxide in sulphuric acid or to the action of sulphuric acid itself on the hydrobromic acid in the strongly acidified solution in the distilling flask.

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[6] Am. Jour. Sci., **27**, p. 174; 1909.

From this it appeared desirable to develop a method which would obtain the vanadium in a solution free from all other metals, so that one might always be certain that the oxidizing or reducing action, whichever is made the basis of a volumetric method, is exerted by vanadium compounds and nothing else. The manner of accomplishing this was suggested in part by a dissertation of Albert Steffan,[7] who used barium carbonate for precipitating vanadium and chromium, together with relatively little iron, from the (ferrous) solution of the steel. The principle at the base of the method has long been applied to other separations. It has invariably been recommended until recently to conduct this precipitation in the cold, shaking frequently and allowing to stand for many hours. It has been found, however, by numerous experiments here, that a few minutes boiling with the carbonate will completely precipitate much larger amounts of vanadium and chromium than are likely to be encountered in steel analysis; furthermore, the precipitates are free from manganese, a distinct advantage from many standpoints over the ether separation. The shortening of the time required for precipitation when solutions are boiled has recently been noted by others in connection with steel analyses; also the use of zinc oxide as a precipitant.[8] The precipitate obtained in this way contains the insoluble matter from the solution of the steel, a little iron, all the chromium and vanadium, and a considerable excess of the precipitant. The vanadium and chromium may be extracted by fusion with sodium carbonate, but the barium holds vanadium tenaciously and more than one fusion is usually necessary, so that this way of handling the precipitate, although apparently simpler, is longer than the one to be described later.

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[7] Ueber die Bestimmung von Kleinen Mengen an Chrom und Vanadin in Gesteinen und Stahlarten, Zürich, 1902.

[8] Slavik, Chem. Ztg., 34, p. 648; 1910.

Smith[9] describes an electrolytic method for separating vanadium from iron by driving the latter into a mercury cathode, and in another section he gives directions for electrolytically precipitating chromium under practically the same conditions; hence it appeared feasible to separate both iron and chromium from vanadium by electrolysis when the three are together. Preliminary experiment showed this to be possible, and it was then decided to dissolve the precipitate mentioned above in appropriate manner and submit it to electrolysis in order to obtain a pure vanadium solution. It seemed desirable, however, to be rid of the excess of the precipitant before electrolyzing. The necessary excess being relatively large, it would take too long to drive the iron and chromium out of solution if the precipitant were to accompany them into solution and be deposited along with them, as would be the case with zinc oxide, for instance. Moreover, it seemed desirable to dissolve the steel in sulphuric acid, as the electrolytic deposition is made from sulphate solution. This, of course, made inconvenient the use of barium carbonate as precipitant. It was therefore decided to try the suitability of cadmium carbonate for the purpose, with the idea of throwing out the excess of cadmium by hydrogen sulphide from the acid solution of the carbonate precipitate. This method gave entirely satisfactory results. The rate of precipitation of the vanadium and chromium seems even more rapid than with zinc oxide or barium carbonate. The precipitate of cadmium sulphide obtained in a boiling, very slightly acid solution is easily filtered and never carries down vanadium.

The precipitation of vanadium and chromium from a reduced and boiling solution of steel by any of the precipitants herein mentioned succeeds equally well in hydrochloric or sulphuric solutions, but seems to proceed a little faster with cadmium carbonate and a sulphate solution.

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[9] Electroanalysis, fourth edition, p. 258.

IV. THE METHOD IN DETAIL

Dissolve 2 to 4 grams of steel in 40 to 60 cc of 10 per cent (by volume) sulphuric acid in a covered 300 cc Erlenmeyer flask. Filter off the insoluble, wash two or three times with water, ignite and fuse for a few minutes with acid potassium sulphate, adding the aqueous solution of the fusion to the main solution. If the steel will not dissolve readily in sulphuric acid, hydrochloric acid may be used, fusing the insoluble as before.[10] Nearly neutralize the solution of the steel with saturated sodium carbonate solution. Then add finely pulverized cadmium carbonate in small portions at intervals of four or five minutes, boiling vigorously between times, keeping the flask well covered. A gram or two of carbonate should remain undissolved at the end of the operation. About fifteen or twenty minutes' boiling always suffices. The time may be even shorter for vanadium steels containing little or no chromium. Allow the precipitate to settle and filter rapidly, so as to prevent oxidation and precipitation of iron on the filter (an 11 cm S. and S. No. 589 white-label filter is recommended). Wash the precipitate twice with hot water; no care need be taken to remove all of it from the flask. Dissolve the precipitate with the minimum of nearly boiling 10 per cent sulphuric acid, catching the filtrate in the flask. Boil to insure solution of material adhering to the sides of the flask. Cool and nearly neutralize with ammonia; there should be no more free acid present than is necessary to prevent the iron from precipitating by hydrolysis when the solution is boiled. Pass a rapid current of hydrogen sulphide for a few minutes while the solution is boiling vigorously. Let the precipitate settle, filter it off, and wash two or three times with hot water. Concentrate the filtrate if necessary and electrolyze in a volume of 60 to 70 cc, using 5 to 6 amperes at 6 to 7 volts. The amount of mercury used in the special apparatus described below was about 200 grams. The solution is tested for iron by ferricyanide; usually when no iron test is obtained all the chromium is removed. However, should there be an unusually large amount of chromium relatively to the iron, this might not happen. In this case the test should be made by removing three or four cubic centimeters of the solution, adding a few drops of hydrogen peroxide and boiling for a few minutes after the brown color, due to vanadium peroxide, disappears. If the solution now remains clear and colorless on adding ammonia, the electrolysis is ended. Acidify the test portion with sulphuric acid before returning it to the electrolyzing apparatus. The simpler ferricyanide test usually answers for all purposes; the complications mentioned earlier, due to reduction of ferricyanide by quadrivalent vanadium, do not interfere in this case, inasmuch as there is no ferric iron to react with the resulting ferrocyanide. When the solution no longer gives a test for iron or chromium, remove it from the apparatus and wash the mercury two or three times with 25 or 30 cc of water while the current is still passing. Add two or three cubic centimeters of sulphuric acid (1–1, by volume), heat to 70° or 80° C, and add permanganate from a pipette until there is a strong pink color. Run sulphur dioxide into the boiling solution for a few minutes; then pass a rapid current of carbon dioxide until the escaping steam gives no test for sulphur dioxide. Filter, preferably through asbestos,[11] or a Munroe crucible, cool the solution to 70° or 80° C, and titrate against $\frac{N}{50}$ potassium permanganate. For extreme accuracy repetition of the reduction and titration is recommended. The reduction may also be made by hydrogen sulphide, if desired.[12] With special facilities a determination may be completed in one and one-half hours, or less.

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[10] In this case the carbonate precipitate must be dissolved in sulphuric acid and the separation repeated in sulphate solution, for the precipitate first obtained contains enough chloride to give trouble if dissolved in sulphuric acid and directly electrolyzed.

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[11] The result will be slightly high if a paper filter is used. This is due to the hydrolyzing and solvent action of the acid solution on the paper (even the best washed filter paper). With alkaline solutions very serious errors may be incurred from ignorance of this fact.

[12] Bleecker, Met. and Chem. Eng., 9, p. 209, Apr., 1911, reduces vanadate solutions electrolytically, using a platinum dish as cathode. This method appears short and simple and might be adopted in many cases. No work has been done here, however, along this line and the exact conditions for complete reduction to the hypovanadate stage, and no further, would probably have to be determined. It is not safe to titrate directly the solution obtained by electrolyzing as described above without the preliminary permanganate oxidation followed by reduction and filtration; to do so usually gives irregular results.

V. NOTES AND PRECAUTIONS

Sufficient exclusion of air is secured by dissolving the steel in a flask kept well covered by a watch glass. The fusion of the insoluble is absolutely necessary, as a large proportion of vanadium remains here; indeed, Nicolardot has proposed methods whereby, with complete exclusion of air, it is possible to secure practically all the vanadium in the insoluble portion when operating on certain classes of materials. This makes a quick and easy qualitative test for vanadium in steel, for as soon as the carbon is burned off the characteristic appearance of the fused vanadium pentoxide is very striking.

The treatment of the insoluble requires but a few minutes. The operations of solution, of cadmium precipitation, and of filtration must be done promptly, for a delay between solution and precipitation gives opportunity for oxidation of iron. This is to be avoided, since it increases the amount of iron going into the carbonate precipitate, thereby prolonging the electrolysis and also interfering with the complete precipitation of the vanadium and chromium. In this latter connection it seems that the particles of carbonate become rapidly coated with the excessive precipitate of ferric hydroxide, and this interferes with their efficiency in neutralizing the solution. The operations of filtering and washing must be particularly rapid. There is no difficulty here if the solution, after boiling, is allowed to stand a few minutes before filtering; the precipitate settles readily and is easily filtered. Two washings with hot water are sufficient. Sometimes a little difficulty is experienced in dissolving the precipitate completely from the filter. This is particularly true if the filtration and washing have not been done rapidly and promptly, giving opportunity for a difficultly soluble coating to form over the surface, due to oxidation and precipitation of iron. However, this trouble will never be serious if the operations are conducted as directed; moreover, even if this iron is not all removed from the filter it is never found to contain vanadium after two or three washings with the dilute acid. The advantage of a carbonate precipitant over an oxide precipitant is shown here, because the carbon dioxide evolved during the process of solution very effectually breaks up the difficultly soluble surface layer, permitting the acid to get at the main body of the precipitate. On the other hand, when using zinc oxide it is often very difficult to dissolve the precipitate with dilute sulphuric acid. The hydrogen sulphide precipitation of the excess of cadmium is accomplished quickly; the solution should be nearly neutralized with ammonia; sodium hydroxide or carbonate should not be used, as in this case sodium would be driven into the mercury during electrolysis, not only prolonging this operation, but introducing other complications. If the degree of acidity is right and a rapid current of hydrogen sulphide is used, the solution being boiled vigorously while this is passing, the cadmium sulphide settles readily and is easy to filter and wash. The solution after filtration can be transferred at once to the electrolytic apparatus, which may have any of the usual forms, such as the convenient small beakers with sealed-in platinum wires at the bottom, described by Smith.[13] If many determinations have to be made, however, the apparatus shown in Fig. 1 has been found very convenient.

The apparatus is a separatory funnel, shown in half size in Fig. 1, with an inwardly projecting tube A. The bore of the stopcock should preferably be as large as shown. A No. 18 platinum wire is sealed in at B. The apparatus is filled with mercury to within 1 or 2 mm of the end of tube A, which itself is completely filled with mercury, and electrical connection is made to the negative terminal of the battery. The anode may have any of the usual rotating forms. The electrolyzing vessel is conveniently supported by an iron ring clamped to the stand carrying the motor for

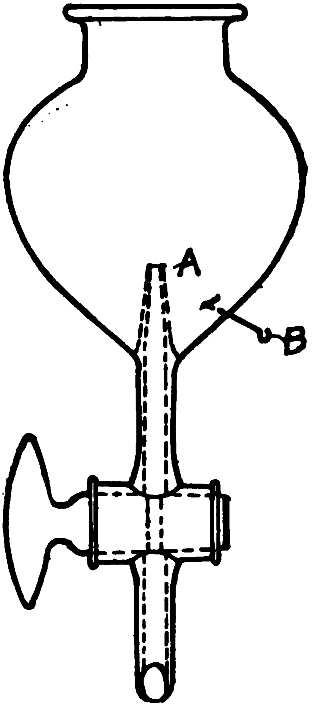

Fig. 1

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[13] Electroanalysis, fourth edition.

rotating the anode. When electrolysis is completed, the anode is brought as close as possible to the surface of the mercury without short-circuiting and the electrolyte is allowed to run out by opening the stopcock. The washing is done very easily by a jet of water from a wash bottle, leaving the stopcock open during the operation, the course of the washing being followed by the ammeter.

If a rotating anode is used, the electrolysis is accomplished in fifteen or twenty minutes. The mercury may be used over and over again without purification. This is another advantage of removing the excess of precipitant before electrolysis, for the amount of foreign material going into it is thus reduced to a minimum. When a stock of mercury saturated with iron and chromium has accumulated it may be purified by the rapid method of Hildebrand.[14] A fair degree of purification can be attained in a few minutes by shaking in a separatory funnel with concentrated hydrochloric acid.

VI. ANALYTICAL DATA

Table I gives some results that have been obtained on synthetic mixtures of chromium, vanadium, and iron. The vanadium was added from a stock solution of sodium vanadate which was carefully standardized by reducing several portions with sulphur dioxide and titrating against permanganate; the iron was from a sulphuric-acid solution of a Bessemer steel with 0.1 per cent carbon, and the chromium from a roughly standardized chrome-alum solution. Precipitation by cadmium carbonate was made in the presence of 4 grams of iron, one-half of the solution of the precipitate being used for electrolyzing.

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[14] Jour. Am. Chem. Soc., **31**, p. 933; 1909.

TABLE I

Number	Vanadium			Chromium
	Present	Found	Error	
1	0.0030	0.0030	0.0000	0.0286
2	.0030	.0030	.0000	.0572
3	.0101	.0102	+.0001	.0358
4	.0117	.0116	−.0001	.0286
5	.0199	.0204	+.0005	.0572
6	.0376	.0371	−.0005	.3150
7	.0407	.0410	+.0003	.3150
* 8	.0010	.0010	.0000	None

* In presence of 10 grams of iron.

Determinations were made on the vanadium steel standard of this bureau, first, from hydrochloric solution; second, from sulphuric solution. Duplicates gave 0.145 per cent vanadium and 0.142 per cent vanadium from the hydrochloric solution. To these there had been added 0.0750 grams and 0.1064 grams chromium, respectively. In sulphuric solution there was obtained 0.145 per cent. The mean of several very careful determinations by bureau chemists, using different methods, was 0.143 per cent. On the new chrome-vanadium standard now in preparation the method gives 0.203 per cent and 0.203 per cent. The averaged complete analysis of the vanadium standard and of the chrome-vanadium standard (full data for the latter have not yet been received and the analysis given is not final) are given below:

TABLE II

Standard	C	Si	P	S	Mn	V	Cr	Ni	Cu	Mo
Vanadium......	0.350	0.303	0.035	0.027	0.669	0.15	0.007	0.009	0.022	0.006
Chrome - Vanadium..........	.377	.113	.043	.029	.58	.197	1.36	.15	.056	......

The results show that a satisfactory degree of accuracy is attainable; this may be increased even more, if desired, by using a larger sample of the steel, for there is no reason why the vanadium should not be concentrated from 10 grams or more of steel, if desired. The minimum amount of vanadium here determined, equivalent to 0.01 per cent in a steel (No. 8 of Table I), shows how delicate the method is; the maximum amount (No. 7 of Table I) shows the possibility of using cadmium precipitation, followed by electrolysis, for high vanadium products. The complete and quick precipitation of large amounts of chromium by cadmium carbonate is equally striking; a method for determining chromium in various kinds of steel, based upon these observations, is being worked out in this laboratory.

From what has been said of the effect of the presence of other substances when titrating hypovanadate solutions with permanganate it is evident that a method like this has distinct advantages in eliminating other metals. If the method is to be used for other steels than those for which it was devised, the effect of other metals must be considered. Such metals as copper and nickel would not interfere. The behavior of molybdenum and tungsten in appreciable amounts has not been investigated, but molybdenum, if at all precipitated by cadmium carbonate, may be eliminated during the hydrogen sulphide precipitation of the excess of cadmium. Tungsten might be removed by evaporation of the cadmium precipitate with nitric acid, followed by filtration. After conversion of the nitrate to a sulphate solution electrolysis could follow as above described. Titanium would probably be precipitated by the cadmium and remain with the vanadium through the electrolysis; however, it would not be reduced by sulphur dioxide or hydrogen sulphide. These points will be investigated as opportunity permits.

VII. SUMMARY

1. Various errors in the usual methods for determining vanadium in steel are pointed out and in a few cases methods for correcting or eliminating these are indicated.

2. A new method based on precipitation of the vanadium by cadmium carbonate, followed by electrolysis, reduction, and titration, is described.

The writer is indebted to Dr. Hillebrand for many helpful suggestions during the course of this investigation.

WASHINGTON, April 24, 1911.

ON THE COMPUTATION OF THE CONSTANT c_2 OF PLANCK'S EQUATION BY AN EXTENSION OF PASCHEN'S METHOD OF EQUAL ORDINATES

By Edgar Buckingham and J. H. Dellinger

1. INTRODUCTION

Planck's equation for the intensity of radiation J, of wave length λ, from a black body at the absolute temperature θ, namely

$$J=\frac{c_1}{\lambda^5\left(e^{\frac{c_2}{\lambda\theta}}-1\right)} \tag{1}$$

or

$$J=c_1\lambda^{-5}\left(1+e^{-\frac{c_2}{\lambda\theta}}+e^{-\frac{2c_2}{\lambda\theta}}+\ldots\ldots\text{etc.}\right)e^{-\frac{c_2}{\lambda\theta}} \tag{2}$$

appears to represent the results of all known observations, nearly or quite within the limits of experimental error. As $\lambda\theta$ decreases, the factor in the parenthesis in equation (2) approaches unity, and the equation tends toward the simpler equation of Wien, or

$$J=c_1\lambda^{-5}e^{-\frac{c_2}{\lambda\theta}} \tag{3}$$

If λ is expressed in microns and θ in centigrade degrees of the standard gas scale, the value of the constant c_2 is in the vicinity of 14400, being apparently between 14600 and 14200. If $\lambda=0.75\mu$, which is about the limit of the visible red, the value of the factor in the parenthesis in equation (2) is about 1.00007 at the melting point of platinum; about 1.006 at the temperature of the arc; and about 1.04 at the apparent temperature of the sun. For decreasing wave lengths, these values approach unity rapidly. For any value of $\lambda\theta$ less than 3000, the value of the factor in the parenthesis is less than 1.01. For visual observations on bodies at temperatures up to that of the arc, the use of Wien's equation as a sufficient approximation to Planck's equation is therefore entirely permissible, and our optical pyrometers are in fact designed on the assumption of the validity of equation (3).

If J_1 and J_2 are the intensities observed, either visually or otherwise, at wave lengths λ_1 and λ_2, when sighting on black bodies at the absolute temperatures θ_1 and θ_2, equation (3) gives us

$$\log \frac{J_1}{J_2} + 5 \log \frac{\lambda_1}{\lambda_2} = c_2 \left[\frac{1}{\lambda_2 \theta_2} - \frac{1}{\lambda_1 \theta_1} \right] \tag{4}$$

If the observations are made at a fixed wave length λ, as through monochromatic absorption glasses or with a spectrophotometer, equation (4) may be reduced to the form

$$\frac{1}{\theta_2} = \frac{1}{\theta_1} + \frac{\lambda}{c_2} \log \frac{J_1}{J_2} \tag{5}$$

by which an unknown temperature θ_2 may be determined from a known temperature θ_1 by observations of J_1 and J_2, if λ and c_2 are known. An instrument for making these observations conveniently at a known wave length in the visible spectrum constitutes an optical pyrometer.

If Wien's equation, together with a certain value of c_2, be assumed, an optical scale of temperature is thereby defined, when a numerical value has been assigned to some fixed reference temperature θ_1. Naturally, however, we desire to adopt such a value of c_2 as shall make this scale agree with the standard gas scale within their common range of about 650° C to 1650° C. The use of the optical scale above the limits of accurate work with the gas thermometer is frequently spoken of as an extrapolation of the gas scale, but it conduces to clearness to regard the optical scale as an independent one which can be and, for convenience, is adjusted to agreement with the gas scale where the two overlap. The accuracy of this adjustment depends on the value assigned to the constant c_2, which is therefore of importance for optical pyrometry in addition to its purely scientific interest.

From equation (4) it is evident that any two observations of the intensity J, at known temperatures and wave lengths, determine the value which c_2 must have in order that equation (3) shall be satisfied. If the observations are made at a fixed wave length and if $\lambda\theta$ is small enough that equations (3) and (2) are sensibly identical, equation (5) or any equivalent equation may be used to find the value of c_2, and the most exact determinations of c_2 have been made in this way, by observations of the so-called isochromatic curves of intensity as a function of temperature with λ constant.

The other most obvious method of determining c_2 is to make the observations at various wave lengths on a body kept at a fixed temperature, i. e., to observe an isothermal or "energy curve" as it is usually called. Virtually all our methods of analyzing the numerical results of observations on black-body radiation are due to Paschen. One valuable method of determining the value of c_2 from an observed energy curve, devised by Paschen[1] before the publication of either Wien's or Planck's equations, was in substance based on the supposition that the equation

$$J = c_1 \lambda^{-a} e^{-\frac{c_2}{\lambda\theta}} \tag{6}$$

of which Wien's equation is a special case, was generally valid. Since the method involves the use of wave lengths so large that Wien's equation is sensibly in error, it does not give constant values of c_2 when used on an accurately observed energy curve, as has been noted by Coblentz;[2] but the method may be so modified as to be applicable to a curve represented by Planck's equation, as will be shown in this paper.

2. THE RELATION BETWEEN THE VALUES OF C_2 AND $\lambda_m\theta$

From equation (3) we get

$$\log J = \log c_1 - 5 \log \lambda - \frac{c_2}{\lambda\theta} \tag{7}$$

and

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[1] Ann. d. Phys. **58**, 455; 1896. Ann. d. Phys. **60**, 662; 1897.

[2] Phys. Rev. **31**, p. 317, Sept., 1910.

$$\frac{d \log J}{d\lambda} = -\frac{5}{\lambda} + \frac{c_2}{\lambda^2 \theta}$$

If λ_m is the wave length at which J is a maximum, we therefore have

$$c_2 = 5\lambda_m \theta \tag{8}$$

If Wien's equation were exact and if the value of λ_m could be precisely determined, for the given temperature, equation (8) would determine the value of c_2. This method, however, can not give accurate results if λ_m has to be determined merely by inspection of the energy curve, because the abscissa of the highest point of the rounded top of the curve can not be determined with any great precision.

Now let a horizontal secant be drawn across the energy curve somewhere below the maximum, and let λ_1 and λ_2 be the wave lengths of the two points of intersection. These values may be read off quite exactly if the secant is drawn at an appropriate height. Equation (7) applied to two *equal* values of J then gives us

$$5 \log \lambda_1 + \frac{c_2}{\lambda_1 \theta} = 5 \log \lambda_2 + \frac{c_2}{\lambda_2 \theta}$$

whence

$$c_2 = 5\ \theta \frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1} (\log \lambda_2 - \log \lambda_1). \tag{9}$$

The application of equation (9) to an observed energy curve constitutes Paschen's method referred to above. If the observed curve were really represented by Wien's equation, equation (9) would give the value of c_2 and, by equation (8), of λ_m, much more accurately than mere inspection of the curve. We have to find how the process must be modified to allow for the fact, shown by equations (2) and (3), that for given values of c_1 and c_2 Planck's curve is everywhere higher than Wien's curve, and that this difference of ordinates increases with the wave length at which the curves are compared.

Let us first find the relation which is satisfied at the maximum ordinate of Planck's curve. By differentiating equation (1) we get

$$\frac{dJ}{d\lambda} = \frac{c_1 \lambda^{-5}}{\left(e^{\frac{c_2}{\lambda\theta}} - 1\right)^2} \cdot \frac{c_2}{\lambda^2 \theta}\, e^{\frac{c_2}{\lambda\theta}} - \frac{5 c_1 \lambda^{-6}}{e^{\frac{c_2}{\lambda\theta}} - 1}$$

and the condition that J shall be a maximum enables us to reduce this to the form

$$c_2 = 5\ \lambda_m\theta\left[1 - e^{-\frac{c_2}{\lambda_m\theta}}\right] \qquad (10)$$

The exponential term is small and we may proceed by successive approximations. Disregarding the correction and setting $\frac{c_2}{\lambda_m\theta} = 5$ we have $e^{-5} = 0.00674$, whence as a second approximation, $\frac{c_2}{\lambda_m\theta} = 4.9663$. A third approximation gives 4.9651, and a fourth does not change these figures. We therefore have for a curve which can be represented by Planck's equation

$$c_2 = 4.965\ \lambda_m\theta \qquad (11)$$

If Planck's equation is a correct representation of the observed energy curve, we can therefore find c_2 from equation (11) by inspection of the curve; but this method is open to the same objection as in the case of Wien's equation, and it is not possible to derive from Planck's equation any exact relation as simple as Paschen's equation (9), by which we may make use of the wave lengths for any pair of equal ordinates. Nevertheless, the importance of the value of the constant c_2 makes it desirable to utilize energy curves as well as isochromatics in determining this value, and to use a more accurate method than that of determining λ_m by inspection.

In the following sections two methods are given for finding the value of c_2 by the method of equal ordinates from an observed energy curve, when the portions of the curve used are representable by Planck's equation. The first of these methods, which is only approximate, is indirect and consists in the substitution in equation (9) of corrected values of the wave lengths read from the energy curve, the point of the method being in the determination of these corrections. It occurred to one of the writers in consequence of a conversation with Dr. W. W. Coblentz, who has already alluded to it.[3]

The second method is based directly upon Planck's equation, and gives a relation similar to equation (9) but with certain correction terms added. These may be computed exactly, but the work may be shortened by an approximation which will be shown to be permissible. This method, which is due to the second of the writers, is simpler in application; at least as exact, even in its approximate form; and altogether preferable to the first method, which retains a value only for checking purposes. Each of the methods presupposes a knowledge of the approximate value of c_2, so that in some cases successive approximations might be necessary.

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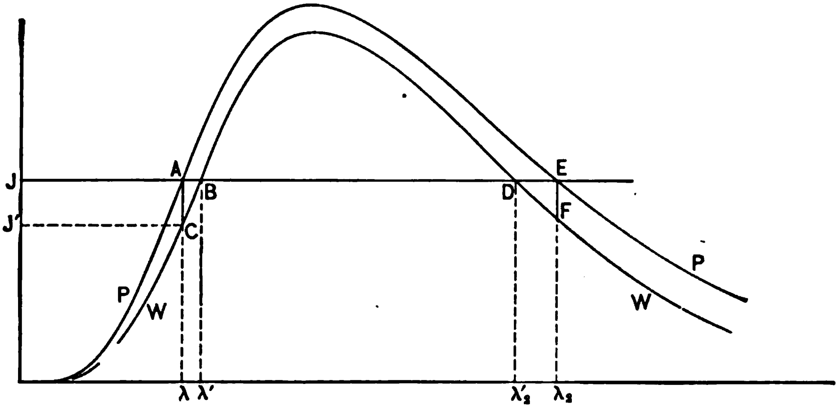
[3] Coblentz, loc. cit. See also Jahrb. der Radioaktivität und Elektronik 8, p. 1; 1911.

3. COMPUTATION OF WIEN'S CURVE FROM AN OBSERVED CURVE

We now assume, as is justified by the experimental confirmations of the validity of Planck's equation, that if the results of accurate observations on $J=f(\lambda)$ at θ constant are plotted, the resulting curve may be represented by Planck's equation with appropriate values of c_1 and c_2. The value of c_1 influences the vertical scale but not the form of the curve, and need not occupy our attention.



Let *PP* in the figure be the observed curve, and let *WW* be a curve plotted from Wien's equation with the same values of c_1 and c_2 that must be used to make Planck's equation represent the observed curve. Let the horizontal secant *ABDE* cut the curves at the wave lengths λ λ' and λ'_2 λ_2. Let J be the ordinate of *A* and J' the ordinate of a point *C* on the Wien curve directly below *A*.

The curves are not far apart and if the secant is not too close to the maximum of the inner curve *W*, the lines *BC* and *DF* may be treated as straight. Considering the triangle *ABC*, we now have

$$\frac{CA}{AB}=\frac{dJ'}{d\lambda}=\frac{J-J'}{\lambda'-\lambda}$$

whence

$$\lambda'-\lambda=\frac{J-J'}{\frac{dJ'}{d\lambda}} \qquad (12)$$

From equations (1) and (3) we have

$$J-J'=c_1\lambda^{-5}e^{-\frac{c_2}{\lambda\theta}}\left(e^{\frac{c_2}{\lambda\theta}}-1\right)^{-1}$$

From equation (3) we get

$$\frac{dJ'}{d\lambda}=c_1\lambda^{-6}e^{-\frac{c_2}{\lambda\theta}}\left[\frac{c_2}{\lambda\theta}-5\right]$$

Substituting these values in equation (12), we have

$$\lambda'-\lambda=\frac{\lambda^2\theta}{\left(e^{\frac{c_2}{\lambda\theta}}-1\right)(c_2-5\lambda\theta)}$$

whence

$$\lambda'=\lambda\left[1+\frac{\lambda\theta}{\left(e^{\frac{c_2}{\lambda\theta}}-1\right)(c_2-5\lambda\theta)}\right] \qquad (13)$$

If c_2 and θ are given, and λ is the wave length of an observed point *A*, equation (13) permits us to find the wave length λ' of the adjacent point *B* at the same height on Wien's curve. The same formula holds for the points *D* and *E* on the long wave length side of the maximum, the sign of the correction term changing when $5\lambda\theta$ passes through the value c_2. This correction term is small and an approximate value of c_2 is sufficient for computing its value unless $c_2-5\lambda\theta$ is small, or λ very large, and in either case the whole reasoning is invalidated because *BC* and *DF* are then no longer sensibly straight.

We have now, in equation (13), an approximate rule by which, from the wave lengths λ_1 and λ_2 at which equal intensities *J* were observed, the values λ'_1 and λ'_2 may be found for two points at the same height on a curve drawn from Wien's equation with the values of c_1 and c_2, which would make Planck's equation fit the observed curve.

For example: Let $c_2=14600$; $\theta=1460°\text{abs.}=1187°\text{C}$; $\frac{c_2}{\theta}=10$. The maximum of the Wien curve lies at $\lambda_m=c_2/5\theta=2$, so that values of λ in the immediate vicinity of 2 must not be used. By equation (13) we get

For $\lambda=$	1	3	5	8
$\frac{\lambda'}{\lambda}=$	1.0000	0.9773	0.9478	0.8921

In general, the value of λ'/λ on the short wave length side of the maximum will be so close to unity that no correction is needed and only the other point need be considered. For a given temperature, the value of λ'/λ may be computed once for all, as is done above for 1187° C, and plotted against λ, so that the correction factor may be read off from this correction curve without a special computation for each point. A series of such curves constructed for different temperatures could be used by interpolation for intermediate temperatures.

Accordingly, if we read from an observed energy curve the wave lengths λ_1 and λ_2 at which the curve is intersected by a horizontal secant, equation (13) permits us to find the wave lengths λ_1' and λ'_2 which would satisfy Wien's equation with the same values of c_1 and c_2 as make Planck's equation fit the observed curve. Substitution of these values in Paschen's equation (9) will then give us the value of c_2, though λ_m for the observed curve is larger than λ'_m for the Wien curve, in the ratio 5:4.965.

4. METHOD OF COMPUTATION INDEPENDENT OF WIEN'S CURVE

If Planck's equation be written in the form

$$J=\frac{c_1}{\lambda^5 e^{\frac{c_2}{\lambda\theta}}\left(1-e^{-\frac{c_2}{\lambda\theta}}\right)} \tag{14}$$

we have

$$\log J.=\log c_1-5\log\lambda-\frac{c_2}{\lambda\theta}-\log\left(1-e^{-\frac{c_2}{\lambda\theta}}\right) \tag{15}$$

and if, as before, a horizontal secant at the height J intersects the observed energy curve at the wave lengths λ_1 and λ_2, equation (15) gives us

$$c_2 = 5\theta\frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1}\Big[(\log\lambda_2-\log\lambda_1)+\frac{1}{5}\log\left(1-e^{-\frac{c_2}{\lambda_2\theta}}\right) - \frac{1}{5}\log\left(1-e^{-\frac{c_2}{\lambda_1\theta}}\right)\Big] \qquad (16)^4$$

Upon comparison with equation (9) it will be seen that the present equation differs from the former by two correction terms of opposite sign. By means of the formula[5]

$$\log\left(1-e^{-\frac{c_2}{\lambda\theta}}\right) = -e^{-\frac{c_2}{\lambda\theta}}-\frac{1}{2}e^{-\frac{2c_2}{\lambda\theta}}-\frac{1}{3}e^{-\frac{3c_2}{\lambda\theta}}-\ldots\ldots\text{etc.} \qquad (17)$$

equation (16) may also be put into the form

$$c_2 = 5\theta\frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1}\Big[(\log\lambda_2-\log\lambda_1)-\frac{1}{5}\left(e^{-\frac{c_2}{\lambda_2\theta}}-e^{-\frac{c_2}{\lambda_1\theta}}\right) - \frac{1}{10}\left(e^{-\frac{2c_2}{\lambda_2\theta}}-e^{-\frac{2c_2}{\lambda_1\theta}}\right)+\ldots\ldots\text{etc.}\Big] \qquad (18)$$

If in (18) all the correction terms after the first are neglected, as will be shown to be permissible, equation (18) enables us to compute c_2 from a preliminary approximate value much more conveniently than was possible by the method described in section 3.

We have now to investigate the error caused by neglecting all the correction terms after the first in equation (18). The error is evidently of the order of the first correction term neglected, inasmuch as the series in equation (17) is convergent for all possible values of λ and θ; the fractional error is therefore of the order of $\dfrac{\frac{1}{10}\left(e^{-\frac{2c_2}{\lambda_2\theta}}-e^{-\frac{2c_2}{\lambda_1\theta}}\right)}{(\log\lambda_2-\log\lambda_1)}$. This expression may be simplified,

---

[4] An equivalent of this form of the complete solution for c_2 has been worked out and used by W. W. Coblentz. In rather complicated form, the solution was given in the Physical Review **29**, 553; 1909. Slight errors which appear in the formula as there printed are corrected in a paper by Dr. Coblentz, to appear in the Physical Review **32**, June–July, 1911.

[5] Peirce's "Short Table of Integrals," formula 768.

since λ_1 is less than λ_2, and in practical cases the second term of the numerator is accordingly small relative to the first, and since, furthermore, it is sufficiently accurate *for this purpose* to set $\frac{c_2}{\theta} = 5\lambda_m$. Hence we may state the fractional error to be of the order of

$$\Delta = \frac{e^{-10\frac{\lambda_m}{\lambda_2}}}{10 \log \frac{\lambda_2}{\lambda_1}} \tag{19}$$

The complete investigation of this expression for the error would require differentiation with regard to λ_1 or λ_2, and this leads to complicated expressions, but it will be sufficient to compute the magnitude of Δ for a few values of $\frac{\lambda_2}{\lambda_m}$. The values computed are as follows:

For $\frac{\lambda_2}{\lambda_m}$ =	1.25	1.5	2.	3.	4.
Δ =	0.00008	0.00017	0.00055	0.0019	0.0036

The values of λ_1 used in the computations were read from a curve representing Planck's equation. It should be noted that the expression for the error, in (19), does not contain the temperature θ, but is determined entirely by $\frac{\lambda_2}{\lambda_m}$ and $\frac{\lambda_2}{\lambda_1}$. Accordingly the error is not different for the curves of different temperatures if we take λ_2 at "corresponding points"[6] of the curves in the sense of Wien's displacement law, i. e., keep the ratio $\frac{\lambda_2}{\lambda_m}$ constant. This does not require that the same λ_2 be taken in computing c_2 from observed energy curves of different temperatures, which would be impracticable on account of the absorption bands not falling at "corresponding points." This discussion relates only to the equality of the errors at "corresponding points."

From a consideration of the errors involved we find that for most practical cases equation (18) may be simplified to the form:

$$c_2 = \frac{\theta\lambda_1\lambda_2}{\lambda_2 - \lambda_1}\left[5\ (\log \lambda_2 - \log \lambda_1) - e^{-\frac{c_2}{\lambda_2\theta}}\right] \tag{20}$$

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[6] See the note at the end of this paper.

which is only slightly more complicated than Paschen's equation itself. The error in this equation is of the same order as that given in (19), viz, less than 3 parts in 1000 for values of λ_2 up to about 3.5 times λ_m. For $\lambda_2 > 3.5\ \lambda_m$ the curve becomes so flat that no accurate readings could be made and the increase of the error beyond this point is of no importance. The best part of the curve to use is that for which λ_2 lies between 1.2 λ_m and 2.5 λ_m, if the temperature is such that no absorption bands affect the experimental determination of this part of the curve.

If the experimental accuracy makes it desirable, the second correction term in equation (18) may be used or the exact equation (16) may be used, but it is doubtful if this will ever be necessary with the present experimental accuracy. In the same way as mentioned above in the discussion of equation (13) the correction to Paschen's equation can be calculated once for all from equation (16) and plotted for future reference. This is, however, hardly necessary, for it would be scarcely any less labor to read the correction from the correction curve than to calculate the exponential term in equation (20) by a slide rule and a short table of exponentials.

5. APPLICATION OF THE FOREGOING RESULTS

The application of the methods developed in this paper may be illustrated by a table of results obtained by readings from an energy curve drawn to represent Planck's equation with the values $\theta = 1442°$ abs. and $c_2 = 14500$, and having its maximum ordinate at $\lambda_m = 2\ \mu$. This curve, which was drawn several years ago, is on a rather small scale, viz, $1\mu = 20$ mm and $J_m = 243$ mm, so that the errors of *reading* from the curve are larger than they would usually be in practice. The readings were made in the vicinity of some of the 14 computed points ($\lambda = 0.5\ \mu$ to $\lambda = 7.8\ \mu$) from which the curve was constructed. They should give the exact values of λ_1 and λ_2 corresponding to the assumed data, $c_2 = 14500$ and $\theta = 1442°$ abs., within about 0.02 μ, except for the last value of λ_2 which may be more in error. On the whole, the accidental errors in the values of λ_1 and λ_2 as read are not unlike what might be expected in the case of an observed energy curve. In order not to give the computations an unfair advantage, the value $c_2 = 14600$ was used as an approximation in equations (13) and (20).

The first and second columns of the table give the pairs of values of λ_1 and λ_2. The third column gives the values of c_2 computed by the Paschen equation (9); the fourth gives the values computed by the method of section 3, using equations (13) and (9); and the fifth those computed by equation (20). The last column gives the values of $(\lambda_2 - \lambda'_2)$ as found by equation (13) and shows the increasing horizontal separation of the Wien and Planck curves with increasing wave length.

1	2	3	4	5	6
λ_1	λ_2	c_2 equ. (9)	c_2 equs. (13) & (9)	c_2 equ. (20)	$\lambda_2-\lambda'_2$
1.54	2.74	14610	14510	14480	0.053
1.30	3.45	14650	14500	14520	0.102
1.17	4.03	14700	14490	14500	0.143
1.03	4.95	14720	14440	14480	0.249
0.85	7.22	14860	14390	14520	0.655

The progressive increase of the values in column 3 shows clearly that Paschen's equation is not applicable to the present curve, drawn from Planck's equation. The values in column 4 are constant within the errors of λ_1 and λ_2 up to about 4.5 μ, or, to $\frac{\lambda_2}{\lambda_m} = 2.25$. Beyond this point they decrease, showing that the assumptions on which the method of section 3 is based are no longer sufficiently exact. The values in column 5 are constant within the errors of λ_1 and λ_2, and give the mean value 14500, showing incidentally that $c_2 = 14600$ was a sufficiently accurate value for use in the computations and that no further approximation is needed unless the values of λ_1 and λ_2 are much more accurate.

6. NOTE ON "CORRESPONDING POINTS"

Wien's displacement law states that if the curve of energy distribution in the spectrum of the radiation from a black body at the absolute temperature θ be plotted with the intensity J as ordinate against the wave length λ as abscissa, the curve for any other temperature θ' may be obtained from the first by: (*a*) multiplying the wave length of each point by $\frac{\theta}{\theta'}$, and (*b*) changing the ordinate of each point in a ratio which is the same for all points but is not specified by this law.

Each point on the first curve is therefore represented by a "corresponding" point on the second. Since $\lambda' = \lambda\frac{\theta}{\theta'}$ or $\lambda'\theta' = \lambda\theta$, we may also define corresponding points on the energy curves for different temperatures, as points at which the value of $\lambda\theta$ is the same. If λ_1, λ_2, and λ_m are the abscissas of any three points on the curve for the temperature θ, and λ'_1, λ'_2, and λ'_m are the abscissas of the corresponding points on that for θ', we evidently have $\frac{\lambda'_m}{\lambda'_1} = \frac{\lambda_m}{\lambda_1}$; $\frac{\lambda'_m}{\lambda'_2} = \frac{\lambda_m}{\lambda_2}$; and $\frac{\lambda'_2}{\lambda'_1} = \frac{\lambda_2}{\lambda_1}$ [see equation (19)]. If λ_m is the abscissa of some point, such as a maximum of J, defined by some analytical condition, corresponding points may also be defined as points of which the wave lengths bear the same ratio to the wave length λ_m on the two curves.

Wien's displacement law makes no reference to the *form* of the function $J = f(\lambda)$; it merely says that any two energy curves for black body radiation may be made identical by plotting wave lengths in units which are proportional to the absolute temperature of the black body emitting the radiation, and then changing the scale of the ordinate J. The change of vertical scale is given by the Stefan-Boltzmann law which states that the area, $J_0 = \int_0^\infty J d\lambda$, of the curve is proportional to θ^4. This requires that the ordinates of corresponding points on two energy curves shall be in the ratio

$$\frac{J'}{J} = \frac{\theta'^5}{\theta^5}$$

Perhaps the clearest representation of the substance of these two laws is by a surface with λ, $J^{\frac{1}{5}}$, and θ as its x, y, and z coordinates. As this surface is swept out by the energy curve, in the form $J^{t} = \phi(\lambda)$, with changing θ, any point on the energy curve describes a curve which lies in a plane containing the λ axis. All the points on this curve "correspond" to one another. The projection of this curve on the λ, θ plane is an equilateral hyperbola since $\lambda\theta$ remains constant.

WASHINGTON, April 26, 1911.

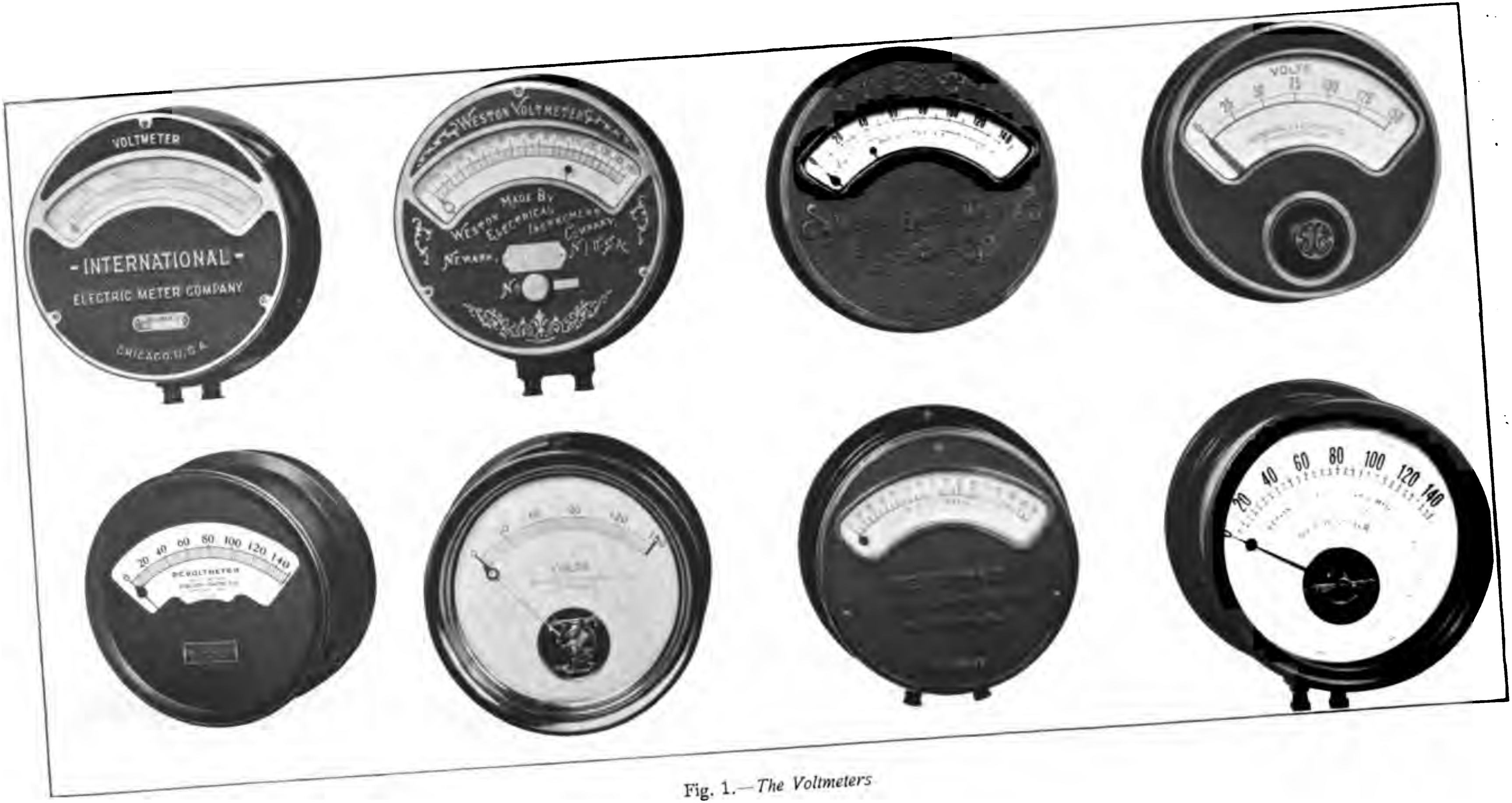

Fig. 1.—*The Voltmeters*

A COMPARISON OF AMERICAN DIRECT-CURRENT SWITCHBOARD VOLTMETERS AND AMMETERS

By T. T. Fitch and C. J. Huber

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I. INTRODUCTION

A comparative test of switchboard voltmeters and ammeters was recently made at the Bureau of Standards for the Bureau of Equipment of the Navy Department. All American makers whose addresses were known, who make instruments of the specified size and type, were given an opportunity to submit instruments. Each of eight different makers submitted a voltmeter and an ammeter. The range of the voltmeters was 0 to 150 volts and of the ammeters

0 to 200 amperes, the latter having separate shunts. As the test was quite comprehensive in regard to this type of instruments, it appears desirable to publish some of the results. A general view of the voltmeters is shown in Fig. 1.

Descriptions of electrical instruments usually give only very general information. For some purposes, however, it is necessary to have at least approximate numerical values of the details of construction and operation of such instruments. For this reason the results of various tests and measurements are given in this article.

The test was divided into two parts—(1) the performance of the instruments, and (2) the determination of their structural constants and dimensions of parts.

The points covered under these two main heads are indicated in the contents, II and III. The test was, of course, carried on separately for the voltmeters and the ammeters. In the figures and tables shown, the voltmeters of the different makers are designated as A, B, C, D, E, F, G, and H. Similarly the ammeters are designated as a, b, c, d, e, f, g, and h, the same letter, capital or small, corresponding to the same maker. The order of the lettering bears no relation to the grouping in the photographic plates.

II. PERFORMANCE OF THE INSTRUMENTS

1. ACCURACY OF CALIBRATION

Figs. 2 and 3 show the errors in calibration of the voltmeters and the ammeters, at room temperatures of 18 and 25° C, respectively. The error at zero refers to the voltage or current indicated on open circuit. A few years ago European makers introduced the use of a zero adjustment on portable instruments and it has since been adopted to a considerable extent by makers in this country. Such an adjustment is also found on the instruments of one maker in this test, and it seems desirable that all should be so provided.

Two other errors are to be looked for in the instrument calibration, the scale error and the adjustment of the sensibility. With the zero in adjustment the instrument can be made to read correctly at any one point of the scale by adjusting its sensibility,

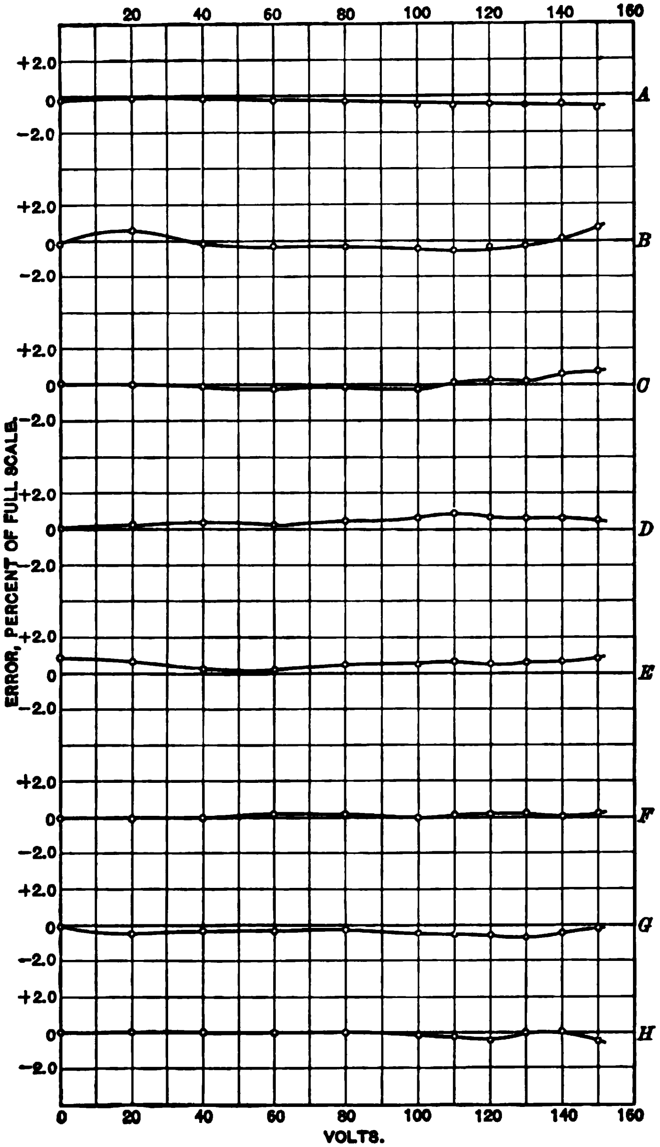

Fig. 2.—*Calibration Curves of Voltmeters*

and if the scale fits the instrument, it will then be correct throughout its range. It is desirable that the flux density in the air gap should be uniform, as in that case the scale will be one of equal divisions. As to making the final adjustment of the sensibility,

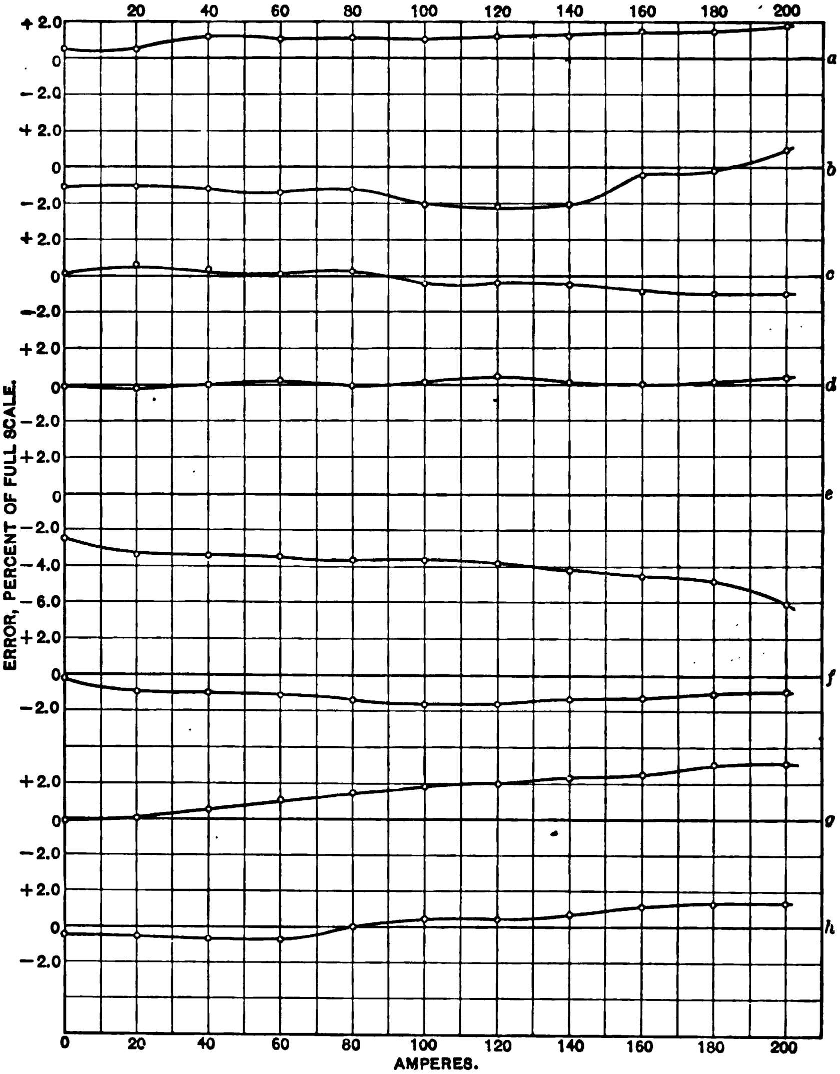

Fig. 3.—*Calibration Curves of Ammeters*

this can be done in several ways. In a voltmeter the strength of the magnets or springs may be changed, or the series resistance may be altered.

In an ammeter the shunt is an additional factor which may be changed. Another method is to shunt the moving coil circuit. In an analogous manner the magnetic circuit may also be shunted by a small piece of iron. While all these methods are used, in practice the one that has been most generally employed is that of altering the series resistance.

It will be noticed that the errors of calibration are small on all the voltmeters, while in the case of the ammeters they are much greater. The irregularities in most of the curves show that the scales do not fit well, aside from the fact that the sensibility is not closely adjusted. Although accuracy is more difficult to obtain in ammeters than in voltmeters, partly owing to the low resistance of the millivoltmeter circuit, still the errors shown on some of these ammeters are excessive, taking into consideration the fact that all were new.

2. RESISTANCE AND POWER CONSUMPTION

In Tables I and II are given the results of the test coming under the remaining headings on performance. The power loss in direct current voltmeters is so small that it is unimportant, although the values vary by a factor of more than two. For ammeters it is of course desirable to have the drop at the shunts as low as is consistent with accuracy of indication. Some engineers specify a drop of from 60 to 75 millivolts at full scale, and it will be seen by reference to the table that good performance, except as to temperature coefficient, can be secured with even less drop than this.

(a) **Shunts—Temperature Effects, etc.**—Another important point is to design the shunts so that the heat developed will be dissipated without an undue rise of temperature. For this purpose the best practice is to use a number of resistance plates connected in parallel between comparatively heavy lugs, with the spaces between the plates open above and below. This facilitates convection currents in the air in carrying away the heat produced in the shunts.

TABLE I

Performance of Voltmeters

Voltmeter	A	B	C	D	E	F	G	H
Resistance (ohms)	12450	16180	18400	7540	12350	14380	16760	14190
Watts at 150 volts	1.81	1.39	1.22	2.99	1.82	1.56	1.34	1.58
Per cent change from standing one hour at 150 volts [1]	−0.2	−0.2	−0.1	−0.1	−0.3	0.0	+0.1	−0.2
Per cent change from reversing a stray field of 4 gausses	0.8	2.2	1.5	1.1	2.5	2.3	1.2	1.7
Damping. Time in seconds to come to rest after closing on 120 volts	0.8	4.8	2.1	1.2	4.6	2.4	2.8	3.7
Mechanical balance. Maximum deviation of index, per cent of full scale [2]	0.0	0.4	0.2	0.1	0.3	0.1	0.1	0.1
Insulation resistance between coil and case, in megohms	>75	15	37	>75	75	>75	25	>75
Temperature coefficient. Per cent change per degree C [3]	−0.01	−0.03	−0.03	−0.02	−0.02	−0.01	+0.02	−0.01

[1] The minus sign indicates that less voltage was required at the end of the period.

[2] In this test the instrument is turned at different angles.

[3] The minus sign indicates that less voltage was required at the higher temperature

TABLE II

Performance of Ammeters

Ammeter	a	b	c	d	e	f	g	h
Resistance of millivoltmeter (ohms)	1.3	3.7	2.7	0.9	2.0	1.3	4.8	3.2
Shunts:								
Millivolts at full load	50	74	60	49	70	50	61	97
Watts loss at full load	10	14.8	12	9.8	14	10	12.2	19.4
Temperature rise in plates at full load °C	53	73	69	38	70	66	62	82
Temperature rise in lugs at full load °C	40	59	58	20	45	58	50	43
Thermal emf. after one hour at full load, millivolts	0.0	0.7	0.0	0.0	0.4	0.3	0.1	0.1
Total change of resistance from 25° to 50° C (per cent) [4]	+0.5	+0.1	+0.2	+0.1	+0.4	0.0	+0.1	+0.1

[4] The plus sign indicates an increase in resistance with rise of temperature.

TABLE II—Continued.

Performance of Ammeters—Continued.

Ammeter	a	b	c	d	e	f	g	h
Per cent change from standing deflected at full load for one hour [5]	−0.5	−1.2	−0.9	−0.1	−1.6	−0.4	−0.3	−0.6
Per cent change from reversing a stray field of 4 gausses	0.7	1.5	1.4	1.1	3.5	1.6	0.8	1.9
Damping. Time in seconds to come to rest after closing circuit on 160 amperes	1.1	2.6	1.6	1.4	5.8	2.1	2.4	2.4
Mechanical balance. Maximum deviation of index, per cent of full scale [6]	0.9	0.7	0.7	0.4	0.6	0.6	0.8	0.7
Insulation resistance between case and coil, in megohms	75	75	37	75	>75	>75	9	75
Temperature coefficient. Per cent change per °C. [7]	+0.11	+0.08	+0.09	+0.15	+0.15	+0.32	+0.28	+0.20

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[5] The minus sign indicates that less current was required at the end of the period.

[6] In this test the instrument is turned at different angles.

[7] The plus sign indicates that more current was required at the higher temperature for the same indication.

3. CHANGE IN INDICATIONS DUE TO STANDING UNDER LOAD—ZERO SHIFT, ETC.

In direct current voltmeters there are two principal causes of change in indications from standing under load—zero shift and change of resistance. None of these voltmeters, however, showed any appreciable zero shift, but they did show change of resistance of the same order as the change in indications.

In direct current ammeters the principal causes of this change are zero shift of the millivoltmeters, the change of resistance, and the thermoelectric effect in the shunts. Where this thermoelectric effect exists, an emf will be found at the shunts after the circuit is opened, due to the extra heating of one junction by the current. The same effect will be produced by any condition which occasions unequal heating of the ends of the shunt, such as a bad contact at one end or a difference in the size of the conductors connected to the shunt.

Table III gives the computed per cent changes due to thermal emf and to heating under full load, compared with the observed change in indication from standing deflected under the same conditions. The computed values are based on the values found separately for the thermal emf of the shunts and their change of resistance under load. It will be noticed that the thermal and heating effects account for most of the change, especially as such instruments can not be relied upon to repeat their readings better than 0.2 or 0.3 per cent. This is partly due to the fact that no parallax mirror is provided in switchboard instruments, and hence the error of reading is greater than in portable instruments of the same type.

TABLE III

Ammeter	a	b	c	d	e	f	g	h
Change due to thermal emf ..Per cent..	0.0	1.0	0.0	0.0	0.6	0.6	0.1	0.1
Change due to heating ....do....	0.8	0.3	0.6	0.2	1.1	0.0	0.2	0.3
Sum ....do....	0.8	1.3	0.6	0.2	1.7	0.6	0.3	0.4
Observed change ....do....	0.5	1.2	0.9	0.1	1.6	0.4	0.3	0.6

4. EFFECT OF STRAY FIELD

To simulate the effect of a stray field a current of 100 amperes was passed through a coil of two turns 62.5 cm in diameter. The instrument under test was placed so that its moving coil was at the center of this external coil, where the magnetizing force in air would be 4 gausses, and with coil and instrument in such relative position that the field due to the external coil was in the same direction as that in the air gap of the instrument. The above field strength is about five times the strength of the earth's field and is equal to the field at a distance of 25 cm from a straight bus bar carrying 500 amperes. As the effect was obtained by reversing this magnetizing force, the change in the field is about ten times the earth's field, or forty times that of the horizontal component, which is usually the only one effective in causing an error. In practice, however, the greatest trouble from stray field is that due to heavy currents in the neighborhood of the instrument. The results of this test are given in Tables I and II. Small fields will produce no appreciable effect when acting at right angles to that in the air gap of the instrument.

5. DAMPING

One of the most important points in the practical use of an instrument is its damping. It is important, not only for the ease and convenience of taking readings, but the accuracy of the readings will often depend upon it. Good damping also reduces the wear on the pivots due to the swing of the pointer with unsteady current or voltage, and it lessens the danger of injury in cases of momentary overload. The universal method used for damping direct-current moving-coil instruments is to wind the coil on an aluminum frame, which acts as a magnetic damper. The amount of damping depends upon the amount of metal used in the frame, the torque, the moment of inertia of the moving element, and the flux in the air gap. In a voltmeter the damping due to the coil itself is negligible, because of the large external resistance in series with it; but in an ammeter it is an appreciable part of the total damping. As a measure of the efficiency of the damping, the length of time required for the needle to come to rest after closing the circuit was measured by a stop watch. The results for the voltmeters are given in Table I, for the ammeters in Table II.

The best-damped instruments come to rest as quickly as an accurate reading can be made, while the more poorly damped ones made seven or eight (single) swings before coming to rest, so that there was a very decided difference in the ease with which readings could be made.

An interesting relation between *damping* and *ratio of torque to weight* is brought out by these instruments, and is discussed later in paragraph III 1b.

6. MECHANICAL BALANCE OF MOVING SYSTEM

For this test the instruments were turned in different positions and the maximum change of position of the index observed. The results are given in Tables I and II.

The moving element is usually provided with two sets of adjustable weights carried on arms placed at right angles. By adjusting these the center of gravity can be brought to the axis.

7. INSULATION RESISTANCE

This test was made with 500 volts direct current applied between case and coils. In Tables I and II the sign > indicates that the resistance was greater than 75 megohms, as that was the limit of sensibility of the apparatus used.

8. TEMPERATURE COEFFICIENT

In the voltmeters the temperature coefficient is a summation effect of the temperature coefficients of the strength of the magnets and springs and the resistance of the coils. In the ammeters there is the added effect of the change in resistance of the shunts. In the voltmeters, which have large series resistances, the principal changes should be those due to the magnets and springs, as resistance materials of negligible temperature coefficient are readily obtainable. The elasticity of the springs has a temperature coefficient of about −0.04 per cent per degree C; that is, they are weaker at higher temperature. The temperature coefficient of the magnets may be plus or minus; but it is usually of the same order and sign as that of the springs, that is to say, the magnetic field is weaker at higher temperatures.

In the tables it is noticeable that the ammeters have a much larger temperature coefficient than the voltmeters. This is due largely to the millivoltmeters, which have a low resistance, a considerable proportion of which is copper. Consequently they have a high temperature coefficient. It is not feasible to wind the moving coil with manganin wire as the resistance would be too high to work on the available millivolt drop unless the design were so changed that more wire could be wound upon it. While it could be made to work in this way, the moving element would be too heavy for good performance. The temperature coefficient could also be greatly reduced by using larger shunts, giving a higher drop, say 200 millivolts; this allows the use of manganin wire in series with the copper coil. As this would increase the cost of the shunts and the power consumption, there is no reason for varying from the present practice, because the temperature errors of switchboard ammeters as now made are of comparatively little consequence.

9. RUGGEDNESS OF MOVING SYSTEM

Both ammeters and voltmeters were tested by reversing the current when standing at full scale deflection. This is a test that such instruments should withstand, and none of those in this test showed any damage from this treatment.

TABLE IV

Moving Elements

	Weight in grams	Full scale torque	Ratio torque to weight	Full scale milliamperes	Number turns in coils	Ampere turns
Voltmeters:		Mm-grams[8]				
A	1.72	9.4	5.5	12.0	69.5	.83
B	3.02	2.9	1.0	9.3	53.5	.50
C	1.64	5.0	3.0	8.1	58.5	.47
D	2.82	21.0	7.4	19.9	103.0	2.06
E	2.88	8.8	3.0	12.1	155.5	1.88
F	3.48	15.0	4.3	10.4	195.5	2.04
G	1.73	2.9	1.7	8.9	45.5	.41
H	3.50	8.6	2.5	10.6	116.5	1.24
Millivoltmeters:						
a	2.55	6.2	2.4	37	11.0[9]	.40
b	4.66	3.7	0.8	20	24.5	.49
c	2.17	3.7	1.7	23	12.4	.29
d	3.26	7.6	2.3	53	13.3	.71
e	3.71	3.1	0.8	36	22.5	.81
f	4.36	6.7	1.5	38	26.5	1.01
g	2.70	2.1	0.8	13	21.5	.28
h	4.60	8.7	1.9	31	36.5	1.13

[8] The centimeter-gram is the unit of torque used by English and German writers.

[9] The effective number of turns is given where several sections were wound in parallel.

III. DETAILS OF CONSTRUCTION

1. THE MOVING SYSTEMS

a. Torque, Weight, Number of Turns.—Fig. 4, shown at the end of this article, is a photograph of the moving elements of the eight different types of instrument, and Table IV gives the numerical constants relating to them. About the only differences between the moving element of a voltmeter and that of a millivoltmeter of the same make are the size and material of the springs and the size of the wire with which the moving coil is wound. The bearing which the ratio of torque to weight has upon the performance is pointed out in the following section. The other factors given in Table IV are of interest, as they show the requirements for the necessary torque.

b. Ratio of Torque to Weight.—Although the importance of the ratio of the torque to the weight of the moving element has often been pointed out, the full significance of this constant is not as generally appreciated as it should be, and unfortunately designers of instruments sometimes allow other considerations to prevent them from keeping this ratio up to a proper value.

The friction between pivots and jewels is proportional to the weight of the moving part, and though this latter is small the area of the pivot which has to carry the weight is extremely small, so that the resulting pressure per unit area becomes very large. In the analogous case of the bearing in a watthour meter Haskins has recently stated that this pressure may reach 200 tons per square inch.[10] An angular displacement of two or three minutes of arc may be detected in the movement of the needle of an instrument, and hence the limiting resisting torque due to the friction of the pivots must be less than the very slight torque obtained by twisting the spring through this very small angle, or the friction will be evident in the motion of the needle. When it is considered that this condition must be maintained under service conditions of wear and vibration, the prime importance of the ratio of torque to weight becomes evident.

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[10] C. D. Haskins: General Electric Review, **13**, No. 9, Sept., 1910.

The weight, full scale torque, and the ratio of torque to weight are given in Table IV both for the voltmeters and the ammeters.

An interesting relation between *damping* and the *ratio of torque to weight* is brought out in Table V, in which the instruments have been given relative ratings for both characteristics, the number 1 indicating the best and the number 8 indicating poorest performance in each case. Such a comparison should, theoretically, be made using ratio of torque to moment of inertia instead of the ratio of torque to weight, but since the coils have the same general shape the moment of inertia may be taken as proportional to the weight.

TABLE V

	Voltmeter								Millivoltmeter							
	A	B	C	D	E	F	G	H	a	b	c	d	e	f	g	h
Rating according to damping	1	8	3	2	7	4	5	6	1	6	3	2	7	4	5	5
Rating according to ratio of torque to weight..........	2	7	4	1	4	3	6	5	1	8	4	2	6	5	7	3

In the case of the voltmeters, the ratings do not differ by more than one except in the case of voltmeter E. This voltmeter has a weak field, and the torque is kept up by using a large number of turns, but the damping is poor, owing to the large moment of inertia and the weak field. Consequently, it is much underdamped, though it has a fairly high ratio of torque to weight.

In the case of the millivoltmeters, g and h show the most difference in the two ratings. They have about the same field strength and the damping is practically the same, but one of them has secured a larger ratio of torque to weight, chiefly by using a larger millivolt drop.

TABLE VI

The Constants of the Magnets

[The dimensions are given in centimeters and the flux densities in gausses per square centimeter]

Millivoltmeter	Length l_m	Cross section q_m	Pole piece surface q_a	Total air gap l_a	$K=\frac{\frac{l_m}{q_m}}{\frac{l_a}{q_a}}$	H Flux density in air gap	Total flux	B Flux density in steel
a	26.4	4.38	11.0	0.260	255	1590	17500	4000
b	25.9	3.94	10.9	.293	246	427	4660	1180
c	34.7	3.02	11.2	.255	505	1450	16200	5400
d	22.4	3.90	9.1	.173	302	2790	25400	6500
e	30.4	2.93	10.6	.450	244	213	2250	770
f	23.7	2.50	11.0	.287	363	875	9630	3800
g	27.7	4.01	8.8	.310	196	551	4850	1210
h	24.7	4.70	13.7	.320	225	740	10100	2200

2. THE MAGNETS—DIMENSIONS, AIR GAP, ETC.

Fig. 5, shown at the end of this article, is a photograph of the magnetic systems of the instruments, and the numerical constants relating to them are collected in Table VI. Tables IV and VI are similar in form to those of Heinrich and Bercovitz in their article on "Die Technischen Messinstrumente" in the Handbuch der Elektrotechnik.

The quantity K appearing in Table VI is the ratio of two ratios; that is, the ratio of the length of the magnet to its cross section divided by the ratio of the length of the air gap to its cross section. Heinrich and Bercovitz divide this ratio K by 100 and call that the safety factor against demagnetization. This is arbitrary, of course, but it is evident that this factor should be large. The values given were taken from the magnets of the millivoltmeters, but they apply also to the voltmeters except, of course, that the flux densities may vary in different magnets.

As the reliability of this type of instrument depends largely upon the permanency of the magnet, it is important that a good magnetic circuit be used. To concentrate the field and make it as uniform as possible, soft iron pole pieces are used with the magnet. The pole pieces used by one maker are merely shells instead of a solid mass of iron. The effect of this is essentially the same as an increase in the air gap, which is, of course, undesirable, as it makes the real permanency factor lower than the value found by the formula. Another maker uses laminated pole pieces. Theoretically this should give better uniformity of field, but in this instance, as the laminations were left unfinished, the lack of uniformity would probably be greater, due to the variations in the length of air gap.

3. MISCELLANEOUS DETAILS OF CONSTRUCTION

A few details of design and construction having to do with convenience in use and reliability of operation deserve to be mentioned.

Legibility of a switchboard instrument is a necessary requirement. Two of the makers have used large figures and heavy lines, making the instruments readily legible at a distance of 20 or 30 feet. The small figures and fine lines used by the other makers cause their scales to be indistinct. There should also be a decided contrast between scale and case for ease in reading. Dull white cardboard scales used with cases of dull black finish gives the best results. The index should be of such shape and size that it may be easily seen at a distance, yet having a sharp tip which can be used for close settings if required. The set index used by two of the makers on their voltmeters is advantageous in keeping a constant setting.

Some makers persist in the use of soft rubber tubing for covering lead wires and terminals. The sulphur used in vulcanizing the rubber attacks the metal. In the case of small wires this often causes a break, while in case of terminals it corrodes the contact surface. In a millivoltmeter the corrosion of contact surfaces is liable to cause the instrument to be seriously in error.

Accessibility for repair is an important point that should be kept in mind by the manufacturers. Although it is desirable that instruments should be repaired by the manufacturers, in many minor defects it becomes quite necessary for an instrument to be repaired at the place of use, and for this reason it should be readily accessible.

In this connection voltmeter H and ammeter h deserve special mention, in that the makers have put a coat of white enamel on the inside of the cases. This not only gives them a neat and trim appearance, but also minimizes the liability of trouble from dirt, fibers, and the like, by allowing such foreign substances to be readily detected.

The word "volts" or "amperes" should be placed on a conspicuous part of the instrument. Its omission often causes trouble for an inexperienced switchboard attendant.

It is to be seen that the general lines of design are very similar in all the instruments, the manufacture having reached the stage where even the general dimensions used are about the same. These instruments may be taken as typical of American direct-current practice, and although no foreign makers were represented in the series of tests, this statement might well be extended to include European practice also. The most decided departure from type is in the use of the single air gap in the case of the instruments of one maker.

Evidently further improvements in direct-current switchboard instruments are to be looked for mainly in the refinement of details of design and construction.

We are indebted to Mr. H. B. Brooks and Mr. P. G. Agnew for many valuable suggestions in connection with this work and to Dr. C. W. Burrows and Mr. R. L. Sanford for some experimental data.

WASHINGTON, March 1, 1911.

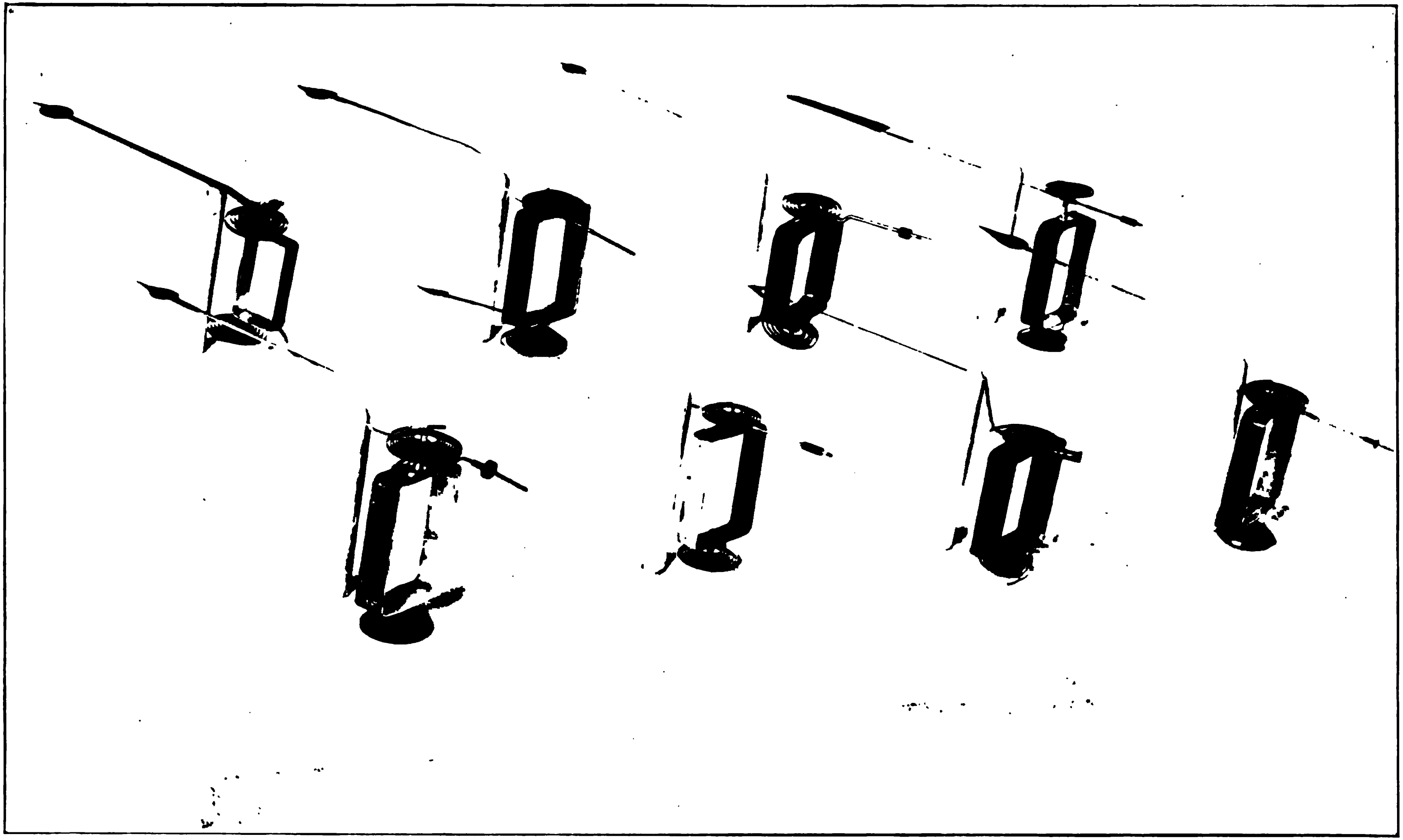

Fig. 4.—*The Millivoltmeter Moving Elements*

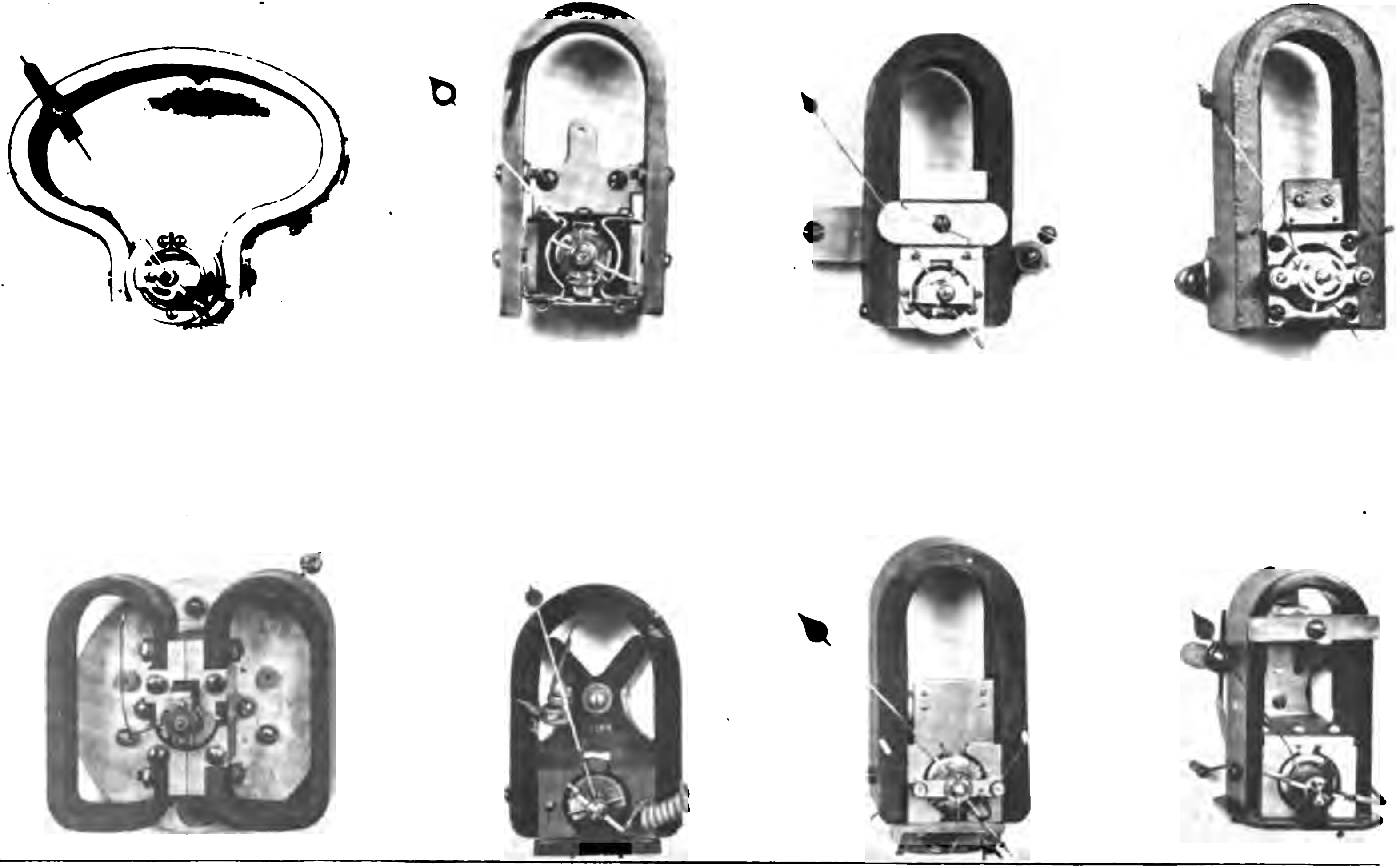

Fig. 5.—*Millivoltmeter Magnets with Moving Coils Assembled*

A STUDY OF THE CURRENT TRANSFORMER WITH PARTICULAR REFERENCE TO IRON LOSS

By P. G. Agnew

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I. INTRODUCTION

In a theoretically perfect current transformer the currents would have a ratio equal to the inverse ratio of turns, and the secondary current would be exactly opposite in phase to the primary current. This ideal condition is shown in Fig. 1, where n is the ratio of turns, and I_1 and I_2 are the primary and secondary currents, respectively.

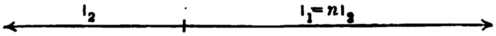

Fig. 1.—*Vector diagram of an ideal current transformer.*

In the actual transformer neither of these conditions is realized, since an appreciable part of the primary current is required to excite the core. Hence, the ratio of the primary to the secondary current is greater than the inverse ratio of turns, and the two currents are not quite in phase but differ by a small angle. (For the case of a leading current in the secondary circuit the ratio may be less than the ratio of turns, but this is a condition which is never met in practice.) A further complication is introduced by the fact that the flux density, and therefore the core loss and magnetizing current are functions of the current, so that in general, both ratio and phase angle are different for different values of the current load. Moreover, the impedance of the instruments connected with the secondary determine, in part, the value of the flux, so that the whole ratio-current curve may be changed by an increase or decrease in the impedance connected with the secondary.

Another possible disturbing factor is wave distortion in the transformer, but it will be shown later that this is entirely inappreciable under practical conditions.

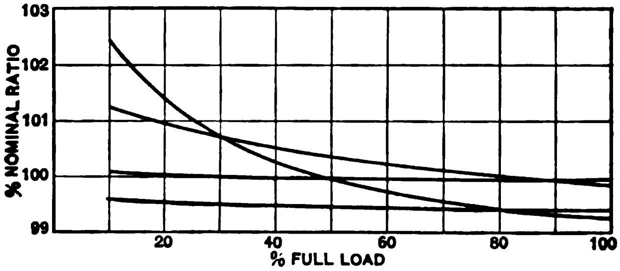

Fig. 2.—*Typical ratio curves.*

Fig. 2 shows some typical forms of the ratio-current curves of current transformers, the ordinates being the ratios (primary to secondary) expressed in per cent of nominal values. Fig. 3 shows a few typical phase angle curves, the ordinates being the angles by which the reversed secondary current leads the primary. These curves as well as those for the ratios are plotted from actually determined values.[1]

It will be seen that both the ratio and the phase angle curves tend to become horizontal straight lines near full load, and that they rise more rapidly toward the low current end of the curve.

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[1] For a considerable number of such curves, giving numerical values, connected load, etc., see:

This Bulletin, **6**, p, 298, 1909, Reprint No. 130.

L. T. Robinson: Trans. Am. Inst. E. E., **28**, p. 1005; 1909.

It is an interesting fact that both types of curves should be so very similar in their general shape.

Although during a considerable experience in the testing of transformers it had been noticed that many transformers showed a tendency to turn down instead of up at the extreme low current end of the ratio curve, these cases had been passed over with the idea that they were probably due to inaccuracies of measurement, since the difficulties in making measurements of high accuracy at currents below about 20 per cent of full load are very great. However, Fig. 4 shows the 25 and 60 cycle ratio curves of a transformer exhibiting unusual and remarkable characteristics. It will be seen that at 60 cycles with the small impedance load used, the ratio increases with increasing current throughout the entire range from 5 per cent of rated load to full load. At 25 cycles the ratio increases with increasing current from the value at low current load to a maximum at approximately half load and then gradually decreases to full load.

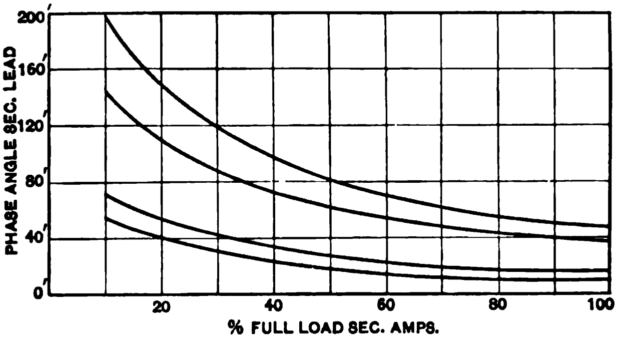

Fig. 3.—*Typical phase angle curves.*

In the 60 cycle curve the total change in the ratio from 10 per cent to full load is 0.23 per cent, a quantity about 10 times as great as the sensibility of the method used, if averaged over the whole range. The experimental evidence that the 25 cycle curve passed through a maximum was equally good. The direct determinations are indicated by circles all lying on the curves in Fig. 4. The points indicated by crosses are computed values which will be discussed later.

Since these measurements were made Edgcumbe has described a transformer showing a maximum in its ratio curve, but otherwise such an anomalous behavior did not seem to have been observed, and it is generally considered by engineers that the ratio always decreases with increasing current. Edgcumbe gave no theoretical explanation of the anomaly.[2] It therefore seemed important to determine if possible whether there might be theoretical errors in the method of measurement used, or, if not, whether some light might not be thrown upon the nature of the iron losses at such low flux densities as are used in current transformers, and upon their possible effect on the ratio and phase angle of the instruments.

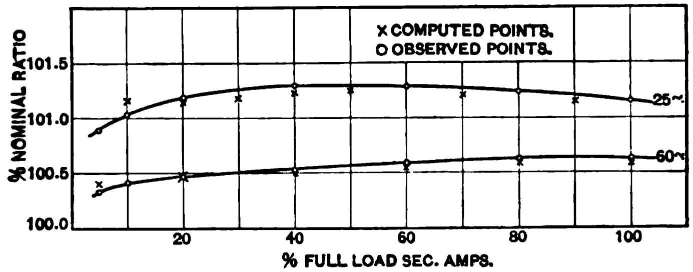

Fig. 4.—*Ratio curves of Transformer F.*

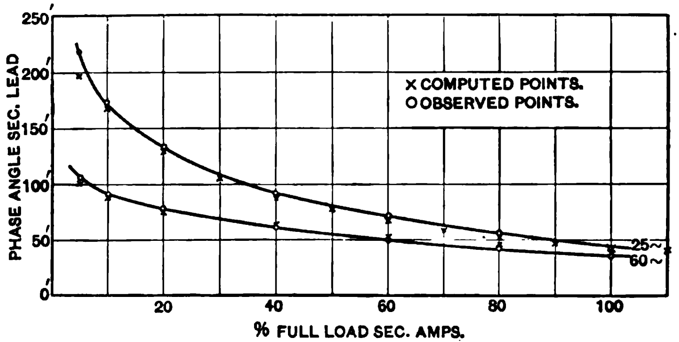

Fig. 5.—*Phase angle curves of transformer F.*

Many other questions in regard to the behavior of the current transformer are involved, such as: the agreement between theory and practice; possible distortion introduced by the transformer itself; the bearing of this upon the definitions of ratio and phase angle involved in different methods of measurement; and the effect of wave form upon ratio. These were necessarily considered in connection with this investigation, as well as with other transformers.

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[2] Elec. Rev. Lond., **67**, p. 163; 1910.

2. METHODS FOR DETERMINING RATIO AND PHASE ANGLE

The most accurate methods for the measurement of ratio and phase angle are null methods depending upon the potentiometer principle. The electromotive forces at the terminals of two non-inductive shunts placed in the primary and secondary, respectively, are opposed; and the resistance of the secondary shunt is adjusted until the in-phase component of the resulting electromotive force is zero. The current relations are shown in Fig. 6. where I_1 R_1 and I_2 R_2 are the electromotive forces, θ the phase angle, and Q the quadrature component of the resultant electromotive force. The method in use at the Bureau of Standards is to place the series coil of an electrodynamometer in series with the primary shunt, and use the moving coil as a detector for setting the in-phase component of the resultant at zero. The complete arrangement is shown in Fig. 7. The switch is thrown to the right and R_2 adjusted for balance; then the switch is thrown to

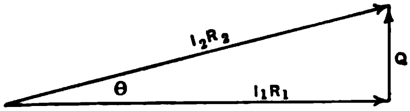

Fig. 6.—*Vector relations in method of measuring ratio and phase angle.*

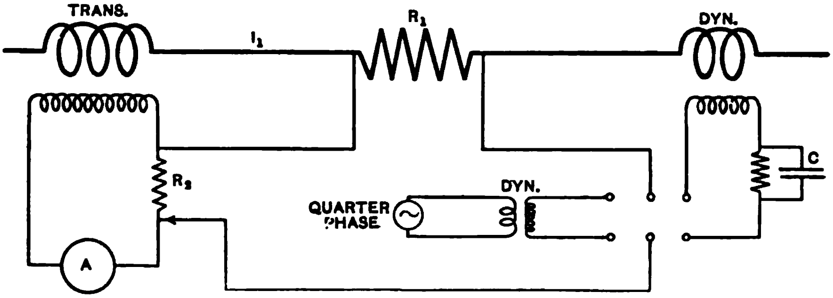

Fig. 7.—*Connections for measuring ratio and phase angle.*

the left, and the deflection due to Q is read. A resistance shunted by a condenser is placed in the moving coil circuit of the series dynamometer so as to make the effective self-inductance of the circuit zero. This avoids a small correction which would otherwise enter.[3] From the values of R_1, R_2 and Q the ratio and phase angle may be readily determined. Unless the inductance of the shunts is negligible, corrections must be made to the phase angle.

Since the method was described a special adjustable noninductive shunt has been designed for use in the secondary. A series of bifilar manganin strips T (Fig. 8), which are silver soldered to the lugs D D, are adjusted to the values 0.025, 0.035, 0.045, etc., ohm. The lugs D D have horizontal amalgamated surfaces which may be clamped by screws to corresponding amalgamated surfaces on the copper blocks C C. Between the blocks B B and C C are two strips of manganin separated by thin mica. The upper one has a resistance of 0.01 ohm, divided into steps of 0.001 ohm, and is connected to the numbered studs. The lower strip has a resistance of 0.001 ohm, divided into 10 divisions, so that by estimating to tenths of a division the resistance may be read to 0.00001 ohm. Copper strips connect the blocks B B to the current terminals A A. The potential terminals are the levers L_1 and L_2, L_1 making contact with the studs, and the end of L_2 sliding on the edge of the thicker manganin strip, which is raised half a millimeter higher than the one to which the studs are connected. The capacity is 10 amperes. At 60 cycles the phase angle is less than one minute.

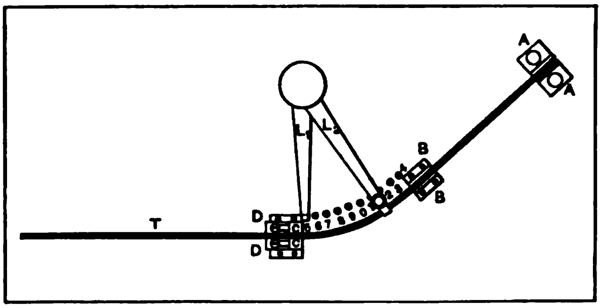

Fig. 8.—*Adjustable noninductive resistance.*

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[3] For a complete description of this method together with a derivation of the equations, see Agnew and Fitch, this Bulletin, 6, p. 292, 1909, Reprint 130.

It has been found that the error introduced by the variation in the resistance of the amalgamated contacts is entirely inappreciable for the accuracy required, which may be taken as one part in ten thousand.

Orlich[4] has described a similar method in which a sensitive electrometer is used as the detector instead of the electrodynamometer.

Robinson[5] has developed a rotating commutator with which he uses a direct current galvanometer as a detector in place of an electrometer or an electrodynamometer. This commutator is driven by a synchronous motor and rectifies the quadrature component Q so that it may be measured by means of a direct-current galvanometer with all the requisite sensibility. The form factor enters into the reduction of the results.

This rotating commutator method has been further developed by Sharp and Crawford,[6] who have also used a mutual inductance in the secondary to reduce the measurement of the quadrature component Q to a null method. They have also suggested a method of using a mutual inductance instead of the shunts in primary and secondary circuits.

Laws[7] has introduced a modification of the two-dynamometer arrangement in order to increase the sensibility at light load, which decreases with the square of the current. He substitutes for the series dynamometer one carrying a constant current which is kept in phase with the primary by an auxiliary device. This difficulty has been overcome in the work at the Bureau of Standards by the use of double-range instruments.

The point has been raised as to whether the two-dynamometer method gives the correct value of the ratio if the possibility of the introduction of distortion by the transformer be taken into account. For example, if we assume that the primary wave is sinusoidal and that the transformer introduces 10 per cent of the third harmonic, then, since this harmonic component of the unbalanced emf Q would give no torque in the dynamometer having a sinusoidal current in its field coil, the ratio of the effective values of the currents would differ from the ratio of the primary and secondary resistances by one-half the square of 0.1, or 0.5 per cent. A similar statement would apply to the measured value of the phase angle.

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[4] Electrotechnische ZS., **30**, p. 468: 1909.

[5] Trans. Amer. Inst. Elec. Eng., **28**, p. 1005; 1909.

[6] Proc. Amer. Inst. Elec. Eng., **29**, p. 1207; 1910.

[7] Elec. World, **55**, p. 223; 1910.

But it is to be noticed that the rotating commutator method gives results which are open to the same theoretical objection, for the null setting gives the condition of equality of mean values rather than the equality of mean effective values. Fortunately the distortion introduced by the transformer is too small to be of any practical significance whatever. Yet it may be well to point out, even though it is of theoretical interest only, that the two-dynamometer method defines the proper ratio to be used in wattmeter measurements, that is the ratio of the primary to the undistorted part of the secondary. This follows from the principle that a harmonic present in the current coil of a wattmeter but not present in the emf wave adds nothing to the torque. This would of course not give the theoretically correct definition for an ammeter, but the accuracy required in alternating current measurements is not as great as that required in the measurement of power. Of course the same considerations hold for the electrometer method since they necessarily define the quantities in precisely the same way.

The phase angle does not suffer the same ambiguity in definition as does the ratio since it is used only in wattmeter or watthour meter measurements. Here the dynamometer and the electrometer methods give the theoretically correct definitions, not taking account of any harmonics that may be introduced by the transformer itself. While the rotating commutator method does include any harmonics introduced by the transformer, and while the percentage error thus introduced into the determination of the phase angle is much larger than in the case of the ratio, this error is still too small to be of practical significance, as will be shown later.

Another objection that has been urged against the rotating commutator method is that the form factor of the current wave used should theoretically be known, but here again the good wave forms given by modern alternators and the specification of practically a sinusoidal wave required in accurate measurements reduce the errors from this source to the limit of experimental error, and they need not therefore be considered.

3. CALCULATION OF RATIO AND PHASE ANGLE

Fig. 9 is a vector diagram of the current transformer. If we let

Φ = flux,
I_1 = primary current,
I_2 = secondary current,
E_2 = secondary electromotive force,
n = ratio of turns of secondary to turns of primary,
φ = phase angle of secondary circuit,
θ = phase angle of transformer,
M = magnetizing current,
F = core loss component of exciting current,
R = ratio of currents,

then we may consider that the flux Φ induces the emf. E_2 in the secondary giving rise to I_2 in the secondary and requiring a component in the primary opposite in phase and equal to $n\ I_2$ in magnitude.

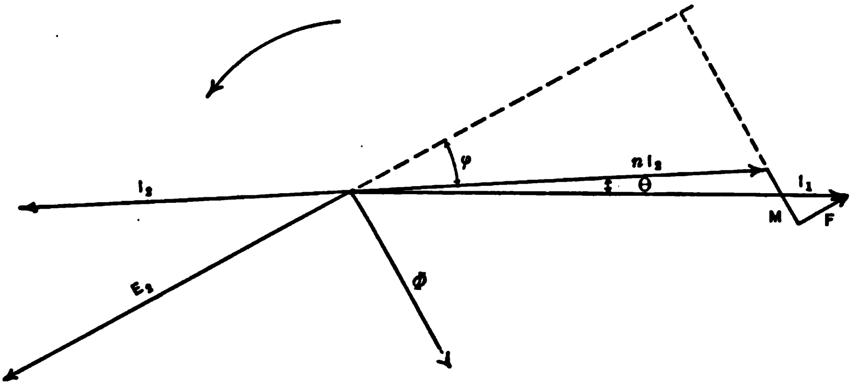

Fig. 9.—*Vector diagram of current transformer on inductive load*

But in order to maintain the flux the primary also has to furnish a magnetizing current M in phase with the flux, and a core loss current F opposite in phase to E_2. Hence, the total primary current is made up of $n\ I_2$, M, and F, taken in proper phase relations.

Projecting the vectors on the line of $n\ I_2$, we have

$$I_1 \cos\theta = n\ I_2 + M \sin\varphi + F \cos\varphi \tag{1}$$

Projecting the vectors perpendicularly to the line of $n\ I_2$ gives

$$I_1 \sin\theta = M \cos\varphi - F \sin\varphi \tag{2}$$

Squaring (1) and (2) and adding, neglecting the terms containing squares or products of F and M,

$$I_1^2 = n^2 I_2^2 + 2\,n\,I_2\,(M \sin\varphi + F \cos\varphi)$$

$$\therefore R = \frac{I_1}{I_2} = \left[n^2 + \frac{2n}{I_2}(M \sin\varphi + F \cos\varphi)\right]^{\frac{1}{2}}$$

$$= n\left(1 + \frac{M \sin\varphi + F \cos\varphi}{n\,I_2}\right) \text{ approx.}$$

$$= n + \frac{M \sin\varphi + F \cos\varphi}{I_2} \quad . \qquad (3)$$

To determine the phase angle divide (2) by (1)

$$\tan\theta = \frac{M \cos\varphi - F \sin\varphi}{n\,I_2 + M \sin\varphi + F \cos\varphi}$$

But as the exciting current is small in comparison to $n\,I_2$, we may write, for the purpose of computing the phase angle where an accuracy of only a few per cent is required

$$\tan\theta = \frac{M \cos\varphi - F \sin\varphi}{n\,I_2} \qquad (4)$$

Formulas practically equivalent to (3) and (4) have been developed by Curtis, Drysdale, and Barbagelata. It has been found that the errors introduced by the approximations made in the derivation may safely be neglected, unless the measurements are carried to extremely low flux densities, but even in this case the uncertainties introduced by the magnetic history of the iron, etc., introduce uncertainties such as to make the use of the exact formula not worth while.

In case the load is noninductive,

$$\sin\varphi = 0 \text{ and } \cos\varphi = 1$$

and (3) and (4) reduce to the forms

$$R = n + \frac{F}{I_2} \qquad (5)$$

$$\tan\theta = \frac{M}{n\,I_2} \qquad (6)$$

and the vector diagram takes the simple form shown in Fig. 10 from which it is seen that the magnetizing current *M* will determine the phase angle, but has very little effect upon the ratio,

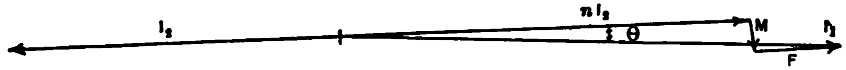

Fig. 10.—*Vector diagram of current transformer on noninductive load.*

while the core loss will determine the ratio, having practically no effect upon the phase angle.

The magnetizing and core loss components of the exciting current were measured directly by a method similar to that described by Sharp and Crawford[8] and shown in Fig. 11. The secondary was adjusted by means of a sensitive reflecting voltmeter which could be calibrated on direct current by throwing the switch S_1.

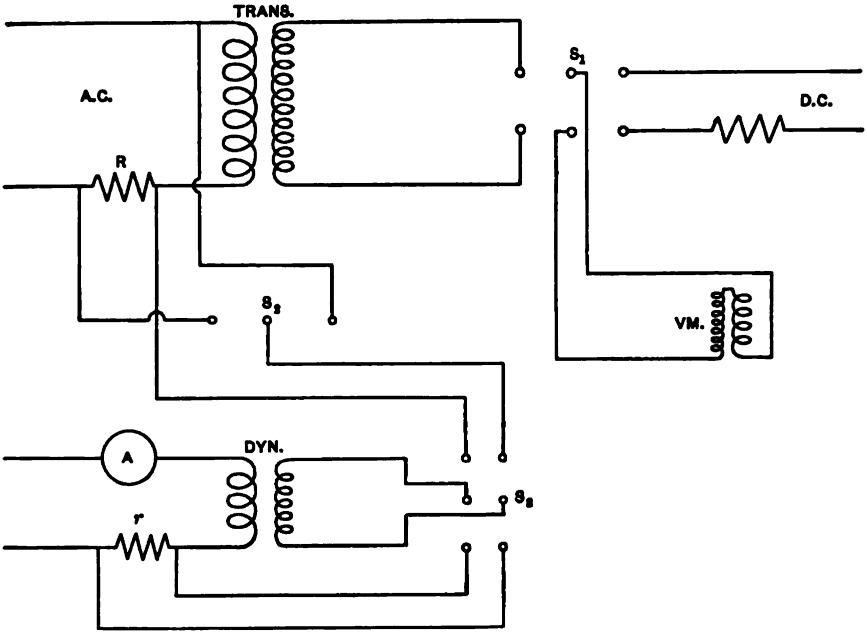

Fig. 11.—*Connections for direct measurement of the magnetizing and core loss components of the exciting current.*

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[8] Proc. Amer. Inst. Elec. Eng., **29**, p. 1207; 1910.

The primary exciting current passed through a shunt R, the emf at the terminals of which could be applied to the moving coil of a dynamometer by closing S_2 to the left, and S_3 up. The field of this dynamometer was excited from a phase shifting transformer.

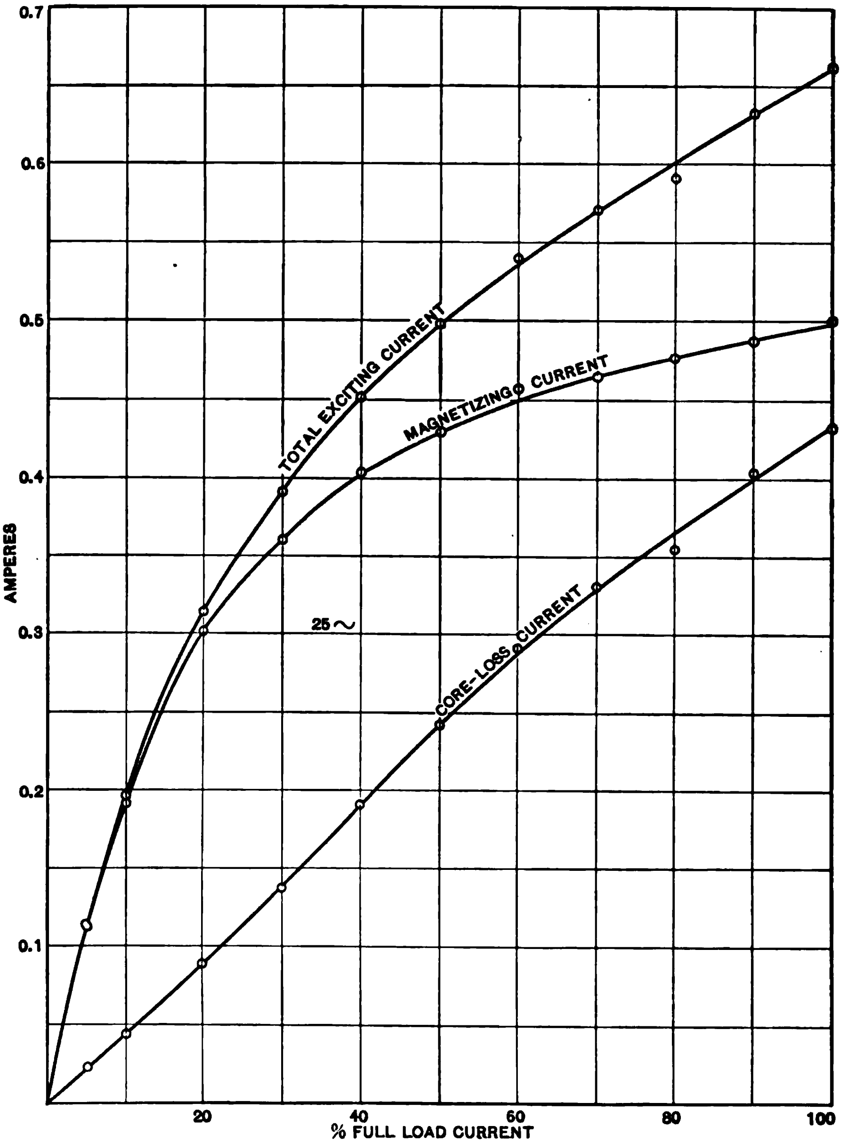

Fig. 12.—*Components of exciting current at 25 cycles. Transformer F.*

The procedure was to throw S_2 to the right, thus applying the primary voltage to the moving coil, and then to adjust the phase transformer until the dynamometer showed no deflection, which indicated that its field was in quadrature with the primary voltage of the transformer, and therefore in phase with the magnetizing current. S_2 was then thrown left and the magnetizing current

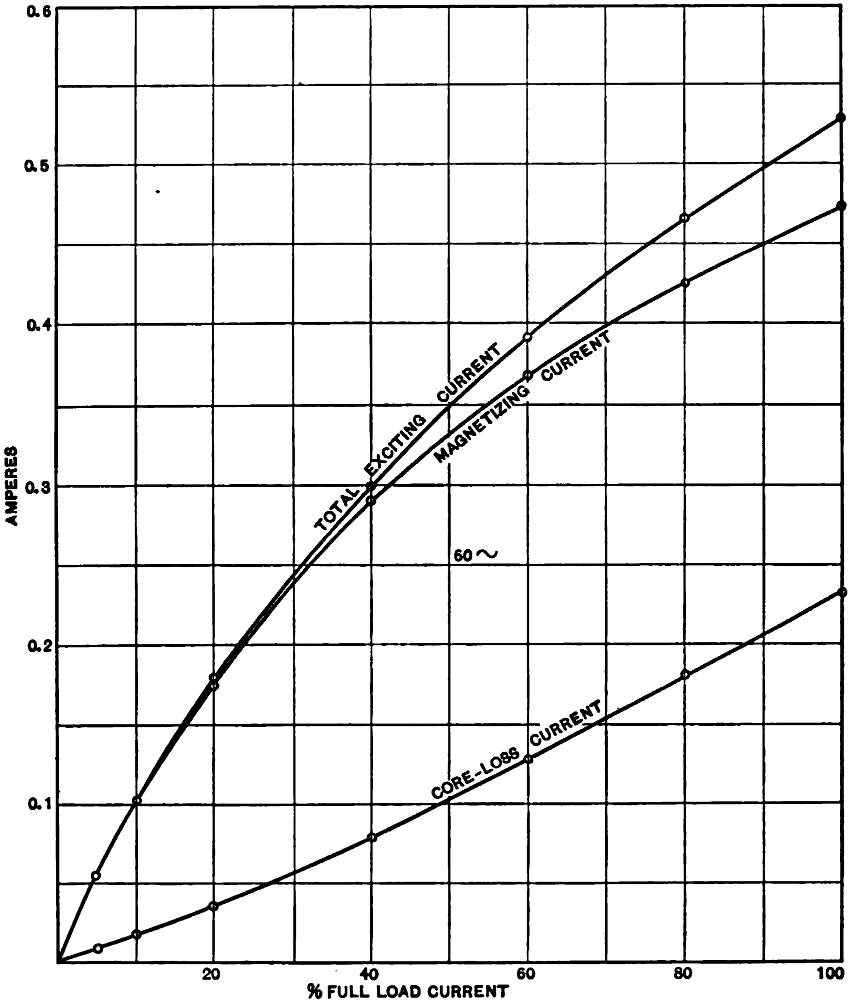

Fig. 13.—*Components of exciting current at 60 cycles. Transformer F.*

read. The phase transformer was then turned through 90° and the dynamometer again read, giving the core loss component. The dynamometer could be calibrated on alternating current by applying the voltage of a shunt r to the moving coil of the dynamometer.

The core loss current, the magnetizing current and the total exciting current at 25 cycles for transformer F are shown in Fig. 12, and the same quantities for a frequency of 60 cycles in Fig. 13.

The ratio and phase angle were computed from this data and the results are indicated by the crosses in Figs. 4 and 5. The core losses at both 25 and 60 cycles are plotted in Fig. 14. The following are the constants of the transformer.

CONSTANTS OF TRANSFORMER F

Number primary turns 25.
Number secondary turns 196.
Rated currents 40 and 5 amperes.
Secondary resistance 0.51 ohm.
Resistance of connected load 0.17 ohm.
Inductance of connected load 0.08 mh.
Maximum flux at 60 cycles, 290.
Maximum flux at 25 cycles, 700.

It will be seen that the agreement between measured and computed values is very good, especially in the case of the 60-cycle curve where the conditions are more favorable. The greatest discrepancy in the range from tenth to full load is but one part in three thousand. Of course, the possibility of the same error entering into both measurements is to be considered, as for example, errors due to wave distortion.

A check measurement of the ratio by an entirely different method was made, using the Northrup hot wire comparator.[9] The makers of the instrument have devised a method for determining the ratio of current transformers, making use of a single potentiometer and a deflection instrument, for holding a direct current through one wire constant while the other wire was thrown from direct to alternating current. But as it was desired to get more sensitive readings than could be obtained by this method, an entirely different arrangement was adopted. The comparator was used as a transfer instrument by which the ratio of the two alternating currents was referred to the ratio of the readings of two potentiometers on direct current. The two hot wires of the instrument, which are indicated by the broken lines in Fig. 15, carry a concave mirror for observation with eyepiece and scale so that

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[9] Trans. Amer. Inst. Elec. Eng., **24**, 741; 1905.

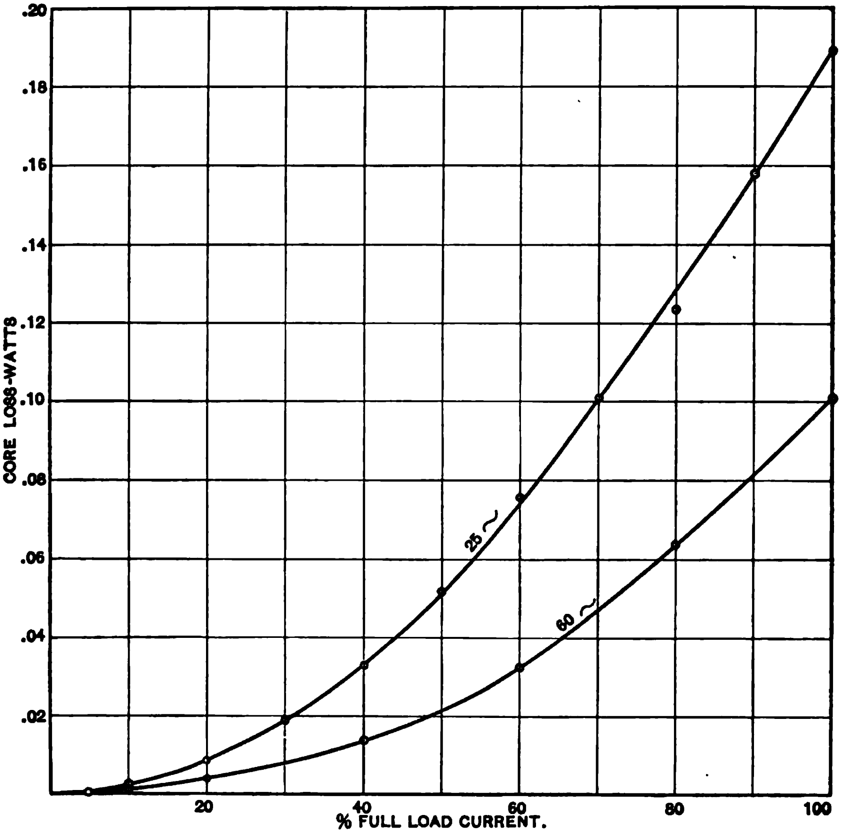

Fig. 14.—*Core loss of Transformer F.*

any difference in the expansion of the two wires gives a deflection of the scale. These were connected in parallel with two shunts R and *r* which could be introduced either in the primary and secondary, respectively, or in two separate battery circuits adjusted to give the same current. The switches were arranged so that the comparator wires could be quickly and simultaneously thrown from alternating to direct current or vice versa. The direct currents were then adjusted so that the comparator showed no change when the switches were thrown in either direction. The direct currents must then be in the same ratio as the alternating currents; and they could be measured by the two potentiometers connected to the resistances R_1 and R_2. Two ammeters A_1 and A_2 were included in the circuits to make it possible to hold the direct current at the same value as the alternating,

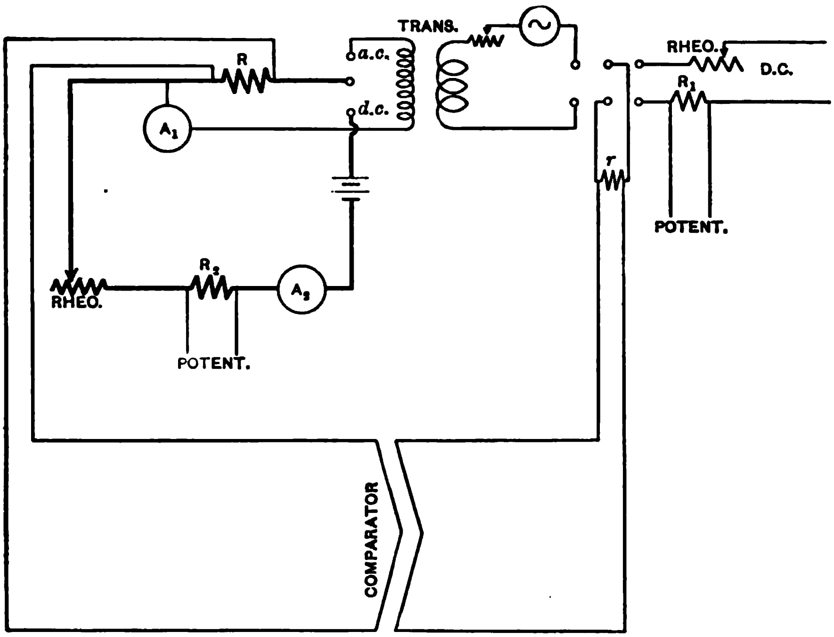

Fig. 15.—*Arrangement for ratio determination by means of the Northrup hot wire comparator.*

in order that the hot wires should be at the same temperature in both cases; but it is to be noted that the final ratio obtained does not depend upon the ammeter readings but upon those of the potentiometers. A further precaution was taken in adjusting a low resistance in the lead to one of the hot wires so that the two wires would expand and contract together when the current was thrown on or off.

The average of 10 measurements gave the same ratio to the last figure (one part in eight thousand), at the full load current as was found by the two-dynamometer null method. (See Fig. 6.) Unfortunately this comparator method did not give great enough a sensibility to allow an adequate check of the values for the ratio at the lower current values. It is very difficult to see how the same error could enter into two such radically different methods of measurement, and as it will be shown that the distortion is negligible, it must be concluded that the forms of ratio curves found for transformer F are correct.

But so close an agreement between observed and computed values indicates that there must be some simple theoretical connection between the nature of the iron losses and the slope of the ratio curve.

4. CONDITIONS FOR LINEAR RATIO AND PHASE ANGLE CURVES

Such a relation may easily be shown to exist if we assume that the *total* iron losses may be expressed in the Steinmetz form

$$W = KB^c \tag{7}$$

where

W = total iron loss in watts
B = maximum flux density
c, K = constants for a given transformer at a given frequency.

If c be assumed to be rigorously constant, it can be shown that the ratio will increase with increasing secondary current when c is greater than 2, and it will decrease with increasing current when c is less than 2, provided the secondary circuit is noninductive. For by (5) the ratio

$$R = n + \frac{F}{I_2}$$

where F is the core loss component of the exciting current and the term $\frac{F}{I_2}$ represents the departure from the ratio of turns. Both the current and the voltage may be taken as proportional to the maximum flux. If E_2 is the secondary voltage then since F is measured in the primary and E_2 in the secondary we have

$$F = \frac{nW}{E_2}$$

and

$$I_2 = B \times \text{Const.} = BK_1$$

$$\therefore \frac{F}{I_2} = \frac{nW}{K_1BE} = \frac{nW}{K_1BK_2B}$$

$$= \frac{nW}{K_1K_2B^2} \tag{8}$$

Hence from (7) and (8)

$$\frac{F}{I_2} = \frac{nKB^c}{K_1K_2B^2} = K_3B^{c-2}$$

$$\therefore R = n + K_3B^{c-2} \tag{9}$$

$$\frac{dR}{dB} = K_3(c-2)B^{c-3}$$

But again, since I_2 is proportional to B,

$$\frac{dR}{dI_2} = K_4(c-2)B^{c-3} \tag{10}$$

This will be positive if c is greater than 2, and negative if it is less than 2. Hence, if the exponent c for the total iron losses is equal to 2, the ratio curve becomes a horizontal straight line. If we assume the eddy-current loss to vary as B^2, then the same conclusions will apply to the hysteretic exponent alone. Formula (9) could readily be put in a form for quantitative determination of the ratio from the core loss by taking the actual value of K_4, but this is not necessary for our present purpose.

Some interesting relations connecting the shape of the ratio curve with the exponent, if the latter be treated as a constant, may be brought out by a development of equation (10). Since the flux may be taken as proportional to the current this may be written

$$\frac{dR}{dI_2} = K_5(c-2)I_2^{c-3}$$

To get the curvature we should, strictly, differentiate this with respect to the length of the curve, but since the curve is nearly horizontal we may, for approximate values, differentiate in respect to I_2 instead.

$$\frac{d^2R}{dI_2^2} = K_5(c-2)(c-3)I_2^{c-4}$$

So that we have

$$\begin{aligned}\text{Ratio} &= n+K\,I_2^{c-2}\\ \text{Slope} &= K\,(c-2)\,I_2^{c-3}\\ \text{Curvature} &= K\,(c-2)\,(c-3)\,I_2^{c-4}\end{aligned}$$

From the last of these equations it may be seen that the ratio curve will be a straight line (zero curvature) only when

$$c=2 \text{ or } c=3.$$

The matter is summarized in the following table.

Exponent	Slope	Curvature	Ratio Curve
$c<2$	−	+	**Slopes down; concave up**
$c=2$	0	0	**Horizontal straight line**
$2<c<3$	+	−	**Slopes up; concave down**
$c=3$	+	0	**Straight line, sloping up**
$c>3$	+	+	**Slopes up; concave up**

The first case is the usual one, well illustrated by the typical curves of Fig. 2. While the straight line of the second case has never been completely realized, it is approached very nearly in some high-grade transformers with low impedance load, (compare the lower curve of Fig. 2). The third case of an upward sloping curve, concave downward is illustrated by the 60-cycle curve for transformer F, (Fig. 4). Neither of the last two cases have ever been observed.

The simple theory as here outlined for a constant exponent is unable to account for a case in which the ratio passes through a maximum, as is the case with the 25-cycle curve for transformer F, (Fig. 4). The slope of this curve will be computed from the results of a more general treatment which will be given later.

It is seen from the factor I_2^{c-4}, which enters the expression for the curvature, that the curvature will in general decrease with increasing current. The typical ratio curve (see Fig. 2) slopes down, is concave up, and the curvature decreases with increasing current, all of which are predicted by theory for the case of an exponent less than 2.

While the case of an assumed constant exponent thus agrees qualitatively with the experimental facts, it is quantitatively insufficient for precise measurements. Moreover, a more serious difficulty lies in the determination of the exponent when the latter is not a constant, and the variation is greater at the low flux densities used in the current transformer.

From the expressions for ratio and phase angle

$$R = n + \frac{M \sin \varphi + F \cos \varphi}{I_2} \qquad (3) \text{ bis}$$

$$\tan \theta = \frac{M \cos \varphi - F \sin \varphi}{n I_2} \qquad (4) \text{ bis}$$

it may be seen that if the permeability were constant and the iron loss exponent were exactly 2, then both the ratio and the phase angle curves would be horizontal straight lines. But this result would be expected since the transformer would then be equivalent to a circuit without iron, which should of course, give a constant ratio and phase angle.

5. EXPONENTS AND THE RATIO OF VARIATION IN IRON LOSSES

It has been assumed in what has gone before that the exponent c is a true constant; otherwise, in differentiating (9) another term containing the derivative of c with respect to B would enter. It has long been known that an equation of the form

$$W = KB^c$$

will not accurately represent either the hysteresis loss or the total iron losses, and so it has become customary to speak of the exponent as varying slightly so as to force the equation to fit the experimental values. Numerous determinations have been published to show that the value of the exponent originally given by Steinmetz of 1.6 is only a sufficiently good mean for use over the limited range of inductions used in the design of power transformers, and that not only different kinds of iron give different values, but that for the same sample of iron the exponent varies with the induction.

Unfortunately, however, the methods that have been universally used to determine the exponent have depended upon the implicit assumption that the exponent is a true constant, and hence the values obtained are not actually exponents, but are, in most cases, the logarithmic derivative of W with respect to B, and this becomes the exponent only in the case where it is a constant. In order to make the matter clear it will be well to consider first the methods that have been used to obtain the exponent from the experimental values.

The method most generally used at present is to plot W against B on logarithmic paper and measure the slope of the resulting curve at various values of B. Still considering c a constant, if we differentiate the equation $W = KB^c$, first taking logarithms of both sides,

$$\log W = \log K + c \log B$$

$$d\,(\log W) = c\, d\,(\log B)$$

$$c = \frac{d\,(\log W)}{d\,(\log B)} \tag{11}$$

which shows that c is the slope of the logarithmic curve. An equally accurate but less convenient method may be used with ordinary cross section paper. Equation (11) may be written in the form

$$c = \frac{\frac{dW}{W}}{\frac{dB}{B}} = \frac{B}{W} \cdot \frac{dW}{dB} \tag{12}$$

from which the value of c at any point of the curve is seen to depend upon the values of W, B, and the slope of the curve at the point. These three quantities must be expressed in consistent units, as the slope $\frac{dW}{dB}$ is no longer a simple geometrical ratio as in equation (11), but has the dimensions of $\frac{W}{B}$. Another method which is often used is to solve for c from the values at two points of the curve. Thus if

$$\left.\begin{aligned} W_1 &= K\,B_1{}^c \\ \text{and} \qquad W_2 &= K\,B_2{}^c \end{aligned}\right\} \tag{13}$$

then

$$c = \frac{\log \frac{W_1}{W_2}}{\log \frac{B_1}{B_2}} = \frac{\log W_1 - \log W_2}{\log B_1 - \log B_2} \tag{14}$$

Common logarithms may be used in either (11) or (14).

None of these methods is correct if we are dealing with a variable exponent for then in differentiating to get (11) and (12) we should have had to take account of the variation of c with respect to B, and evidently (14) could not have been deduced at all since we should have had different values of c in (13). This will appear more clearly in an examination of the general case in which

$$W = K\,B^z \tag{15}$$

where the exponent z is now a variable. It may first be said that suggestions have been made that K should be considered to vary so as to fit the observations to some sort of a curve, and some writers have even treated both the coefficient and the exponent as variables, which is manifestly absurd. To consider that we have an exponent which varies slightly about a mean introduces complications, as will be shown, which greatly limits its usefulness, while any attempt to treat such a formula containing a variable coefficient can accomplish nothing since in its very simplest form the exponent would reduce to unity which merely brings us back to the measured values of B and W.

To determine, then, the relations which follow by treating the coefficient as constant and the exponent as a variable, write (15) in the logarithmic form,

$$\log W = \log K + z \log B$$

Differentiating,

$$\frac{dW}{W} = \log B\,dz + z\,\frac{dB}{B}$$

$$\frac{\dfrac{dW}{W}}{\dfrac{dB}{B}} = z + B \log B\,\frac{dz}{dB} \tag{16}$$

The left-hand member of this equation is the logarithmic derivative of W with regard to B, or the slope of the curve obtained by plotting W against B on logarithmic coordinate paper. If z is a constant the last term becomes zero, the curve becomes a straight line, and the slope of the logarithmic curve is the exponent. But if z is not zero the value of the exponent from equation (16) is

$$z = \frac{\dfrac{dW}{W}}{\dfrac{dB}{B}} - B \log B\,\frac{dz}{dB} \tag{17}$$

This shows that *the logarithmic derivative is not the same as the exponent*, as is tacitly assumed in the methods in common use in the determination of the exponent where the latter varies. The last term in (17) is entirely neglected in the methods which make use of either logarithmic or ordinary coordinate paper, as what is measured in these cases is merely the logarithmic derivative. Similarly the method of solving for the exponent by using values at two points of the curve will not give even the average value of the exponent over the range taken, as it is generally believed to do, for by equation (14) the quantity thus given is

$$\frac{\log \frac{W_1}{W_2}}{\log \frac{B_1}{B}}.$$

Now, if we take B_2 very near B_1 we may replace W_1, W_2, B_1, B_2, by $W+\delta W$, W, $B+\delta B$, and B.

$$\frac{\log \frac{W_1}{W_2}}{\log \frac{B_1}{B_2}} = \frac{\log \frac{W+\delta W}{W}}{\log \frac{B+\delta B}{B}}$$

$$= \frac{\log\left(1+\frac{\delta W}{W}\right)}{\log\left(1+\frac{\delta B}{B}\right)}$$

and we may replace $\log\left(1+\frac{\delta W}{W}\right)$ by $\frac{\delta W}{W}$, which is the first term in its expansion, and similarly for B. This gives

$$\frac{\frac{\delta W}{W}}{\frac{\delta B}{B}}$$

which is the logarithmic derivative. Hence, this method gives a result which approaches that given by the other methods, namely, the slope of the logarithmic curve instead of the exponent.

The slope of the logarithmic curve is, however, of much more practical importance than the true exponent, for the greatest use of such empirical relations is as interpolation formulas. And the logarithmic derivative is an exceedingly convenient form for interpolation, since for small variations it is the ratio of the percentage change in the dependent variable to the percentage change in the independent variable. The same confusion of it with a true exponent has developed in many similar experimental relations, such as, for example, the variation of the candlepower of lamps with voltage or with current or with the power supplied, and the variation of the resistance of fluids to objects moving through them. Such a confusion of terms is very unfortunate since it may lead to wrong conceptions. For example, in the case of incandescent lamps some of these logarithmic derivatives have numerical values very near the exponents in some of the theoretical radiation formulas, and it is misleading to express the relationship in exponents or powers of the dependent variable when the approximate agreement in numerical values may be entirely accidental.

It seems, therefore, advisable to have some simple expression which will of itself convey the meaning and be free from the objections that have prevented the common use of the term "logarithmic derivative", and I shall hereafter refer to this quantity as the "ratio of variation". For the suggestion of this term I am indebted to Mr. C. E. van Orstrand.

In order to bring out graphically the differences that may exist between the exponent and the ratio of variation in geometrical curves of the general parabolic form and whose exponents are of the order of magnitude of those met with in iron losses, in Fig. 16 the curve $y=x^{2+\frac{1}{x}}$ together with the exponent and the ratio of variation have been plotted. This curve was chosen as the values of the exponent and the ratio of variation are around 2 and both decrease with increasing values of x, for it is to be remembered that by equation (10) the ratio curve of the current transformer has its slope determined by the exponent of the total iron losses, provided that exponent is constant. It will be shown later that the same statement will hold when the exponent is not constant if we use the ratio of variation instead of the exponent. In Fig. 17 the curve $y=x^{1+0.1x}$ together with the exponent and the ratio of variation are plotted. It will be seen that when the exponent is 2 the ratio of variation is 4.3. It happens that the curve for the ratio of variation for this purely mathematical curve is very much like one recently published for the hysteretic exponent for silicon steel at high inductions in which values as high as 3.6 were given,[10] but as the method used in determining the "exponent" was to take the slope of the loss curve plotted on logarithmic coordinate paper, evidently the quantity actually determined was the one here designated as the ratio of variation. Very probably the exponent as determined by methods to be explained presently would not have been greater than 2. The data given were insufficient to determine this point.

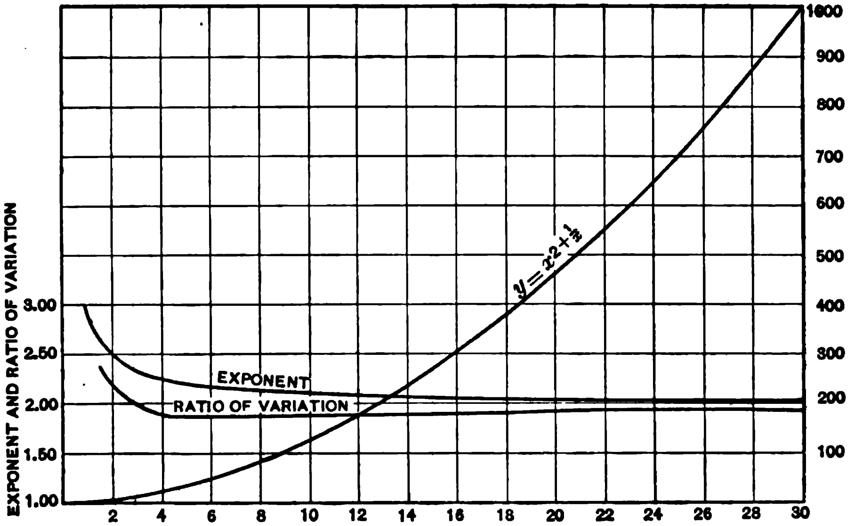

Fig. 16.—*Showing the difference between the exponent and the ratio of variation in the curve* $y=x^{2+\frac{1}{x}}$

Since the last term in equation (16) is positive it follows that the ratio of variation will be greater than the exponent when the latter

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[0] W. J. Woolridge, Proc. Amer. Inst. Elec. Eng., **30**, p. 139, 1911.

is increasing, and less when the exponent is decreasing. Consequently the exponent curve lies above in Fig. 16 and below in Fig. 17.

If in the case of a curve whose exponent is changing slowly we choose two points of reference and solve for the exponent as if it were constant, one might expect to get a value somewhere near the mean of the actual values at the given points, but such is not the case. It may be either greater or less than the actual value at either limit, according to circumstances. A more surprising result of the variation of the exponent is the effect that such a method has in making large changes in the coefficient. For example, if we consider the curve of Fig. 17 as an experimental curve and

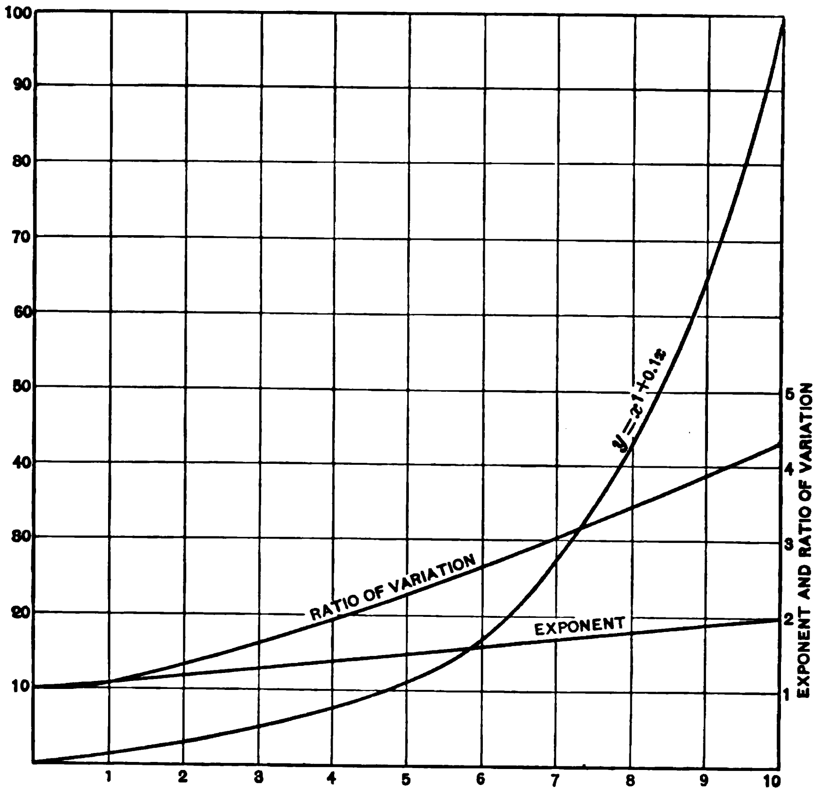

Fig. 17.—*Showing the difference between the exponent and the ratio of variation in the curve* $y=x^{1+0.1x}$

attempt to determine the coefficient and exponent by this method, which is the one that has been most frequently used in discussing changes in the Steinmetz exponent, we get the following results. The computed exponents are nearly identical with the ratio of variation:

Limits used	**Actual curve at midpoint of range**	**Computed equation**
$x=6$ to $x=8$	$y=x^{1.7}$	$y=0.075\ x^{3.05}$
$x=8$ to $x=10$	$y=x^{1.8}$	$y=0.0137\ x^{3.86}$

The matter is not, however, so serious as these results indicate at first sight, for while the exponents have increased the coefficient has changed from unity to the small fractions, and either of the computed curves will give fair approximations throughout the small range for which it is computed. Yet it does emphasize the desirability of abandoning the use of the word "exponent" as applied to the results of such processes.

There are special cases in which the exponent may be determined with a fair degree of accuracy. If the ratio of variation is found to be constant over a range large enough to make sure of its constancy, it is in this region also the true exponent, and the coefficient may be calculated; and its value may be used in calculating the exponent at any other point of the curve. Also if the ratio of variation passes through either a maximum or a minimum its value at this point is the exponent, for a maximum or minimum in the ratio of variation means a point of inflection on the logarithmic curve, the condition for which is

$$\frac{d^2\,(\log y)}{d\,(\log x)^2}=0$$

$$\frac{d\,(\log y)}{d\,(\log x)}=c$$

$$d\,(\log y)=cd\,(\log x)$$

$$\log y=c\log x+\log K$$

$$=\log K\,x^c$$

$$y=Kx^c$$

Now if we consider the exoonent at the point $(x_0\ y_0)$ to be determined, then

$$\frac{y}{y_0}=\frac{Kx^z}{Kx_0^{z_0}}$$

From which

$$z=\frac{\log y+Z_0\log B_0-\log y_0}{\log B} \tag{18}$$

and

$$K=\frac{y_0}{x^{z_0}} \tag{19}$$

By this method the exponent has been computed for the 25-cycle core loss curve of transformer F (Fig. 18). The exponent is very much more nearly constant than the ratio of variation. In order to get an idea of the change of the exponent and of the ratio of variation over a wide range of flux densities the core loss data, determined by Mr. C. J. Huber on 2 special transformers, are platted on logarithmic paper in Fig. 19. The cores were of ring stampings of ordinary transformer steel, and the determinations were made by the wattmeter method at both 30 and 60 cycles. The core was first carefully demagnetized and the measurements made in the order of increasing flux.

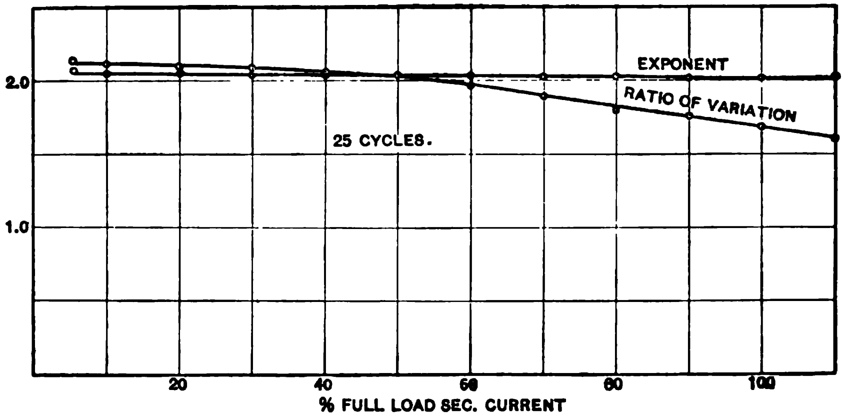

Fig. 18.—*Exponent and the ratio of variation for transformer F.*

The core of transformer S_1 was ordinary transformer steel, while that of S_2 was a silicon steel. The observed values of the total iron losses are given in Table I. The ratio of variation of the core loss of these transformers at 30 and at 60 cycles is plotted in

Figs. 20, 21, 22, and 23. Taking the ratio of variation as constant at 4000 lines, the exponents have been calculated by formula (18)

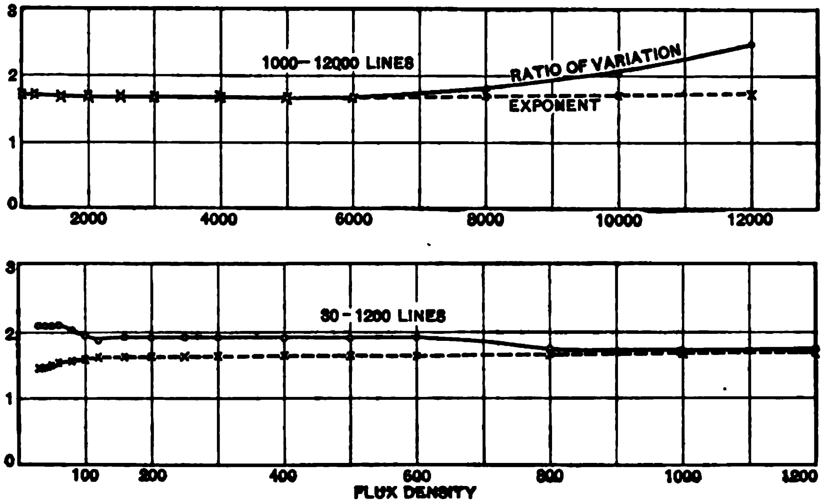

Fig. 20.—*Exponent and ratio of variation for core loss of transformer S_1 (ordinary steel) 60 cycles.*

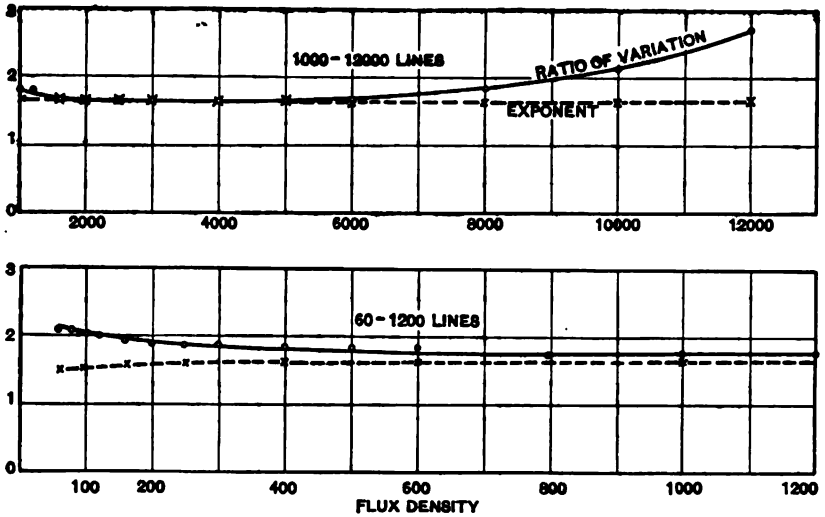

Fig. 21.—*Exponent and ratio of variation for core loss of transformer S_1 (ordinary steel) 30 cycles.*

and the results plotted in the same figures. It is evident from the curves at high flux densities the ratio of variation reaches very high values for both the silicon and the ordinary steel, while the change in the exponent above 2000 lines is extremely slight. The exponent is more nearly constant than the ratio of variation, and after assuming a value at some given point may be determined with a much greater relative accuracy. To bring this last fact out more clearly the computed values are given in Table II.

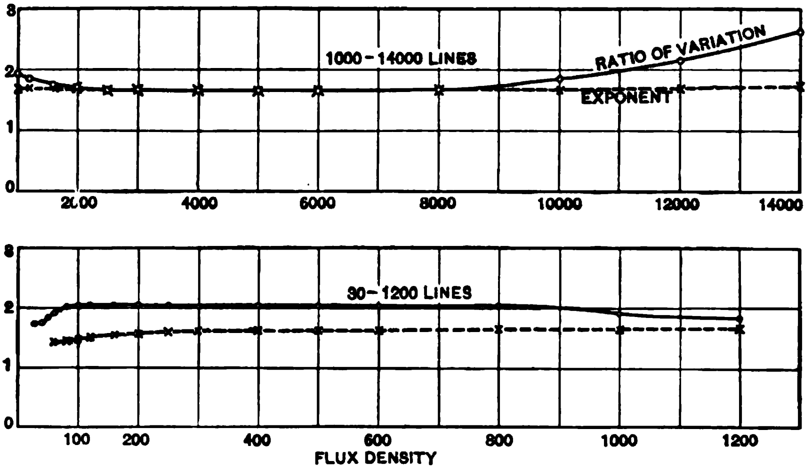

Fig. 22.—*Exponent and ratio of variation for core loss of transformer S_3 (Silicon steel) 60 cycles.*

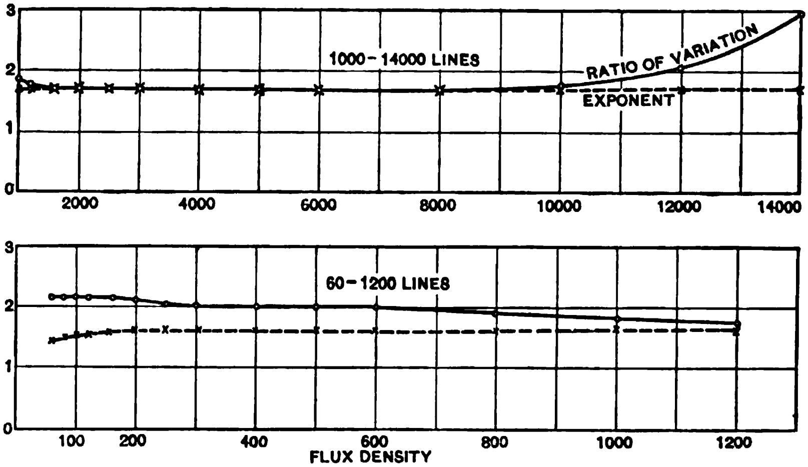

Fig. 23.—*Exponent and ratio of variation for core loss of transformer S_3 (silicon steel) 30 cycles.*

TABLE I

Total iron losses (Watts per Kg)

Flux	Transformer S_1, ordinary steel		Transformer S_2, silicon steel	
	30~	60~	30~	60~
30		0.000080		0.000040
40		.000145		.000050
50		.000235		.000092
60	0.000158	.000353	0.00006	.000135
80	.000294	.000632	.00011	.000256
100	.000458	.000971	.00018	.000390
120	.000666	.00139	.00027	.000570
160	.00116	.00242	.00052	.00103
200	.00179	.00375	.00079	.00167
250	.00272	.00585	.00126	.00270
300	.00385	.00807	.00185	.00385
400	.00653	.0140	.00330	.00694
500	.00985	.0214	.00518	.0109
600	.0140	.0298	.00762	.0154
800	.0233	.0505	.0131	.0271
1000	.0344	.0751	.0199	.0418
1200	.0468	.104	.0282	.0590
1600	.0757	.171	.0465	.0993
2000	.108	.248	.0680	.147
2500	.154	.358	.0988	.214
3000	.207	.484	.133	.290
4000	.324	.776	.210	.464
5000	.466	1.14	.302	.676
6000	.630	1.55	.406	.914
8000	1.15	2.56	.671	1.48
10000	1.73	3.92	.980	2.20
12000	2.56	6.14	1.39	3.11
14000	4.12	9.42	2.05	4.73
16000	5.02		3.01	6.83

TABLE II

Exponents

Flux density	Silicon steel (S_8)		Ordinary steel (S_1)	
	30~	60~	30~	60~
30		1.36		1.49
40		1.32		1.48
50		1.40		1.51
60	1.45	1.43	1.49	1.55
80	1.50	1.49	1.49	1.58
100	1.53	1.50	1.51	1.60
120	1.55	1.53	1.53	1.61
160	1.60	1.56	1.56	1.63
200	1.61	1.58	1.57	1.64
250	1.63	1.60	1.58	1.65
300	1.64	1.62	1.59	1.66
400	1.66	1.64	1.60	1.67
500	1.67	1.65	1.61	1.68
600	1.68	1.66	1.62	1.68
800	1.70	1.67	1.63	1.69
1000	1.70	1.68	1.63	1.69
1200	1.70	1.68	1.63	1.69
1600	1.71	1.69	1.64	1.70
2000	1.71	1.70	1.63	1.69
2500	1.70	1.69	1.63	1.69
3000	1.70	1.69	1.63	1.69
4000	1.70	1.69	1.64	1.69
5000	1.70	1.69	1.63	1.69
6000	1.70	1.69	1.63	1.69
8000	1.70	1.69	1.65	1.70
10000	1.70	1.69	1.65	1.70
12000	1.70	1.69	1.66	1.71
14000	1.71	1.71	1.68	

The ratio of variation is, of course, independent of the units in which W and B are expressed, but the exponent is dependent upon the units used for B although it does not depend upon the units in which W is expressed. For, if instead of B we write αB_1, where α is a constant, the equation

$$W = K B^z$$

becomes

$$\begin{aligned} W &= K (\alpha B_1)^z \\ &= K\alpha^z B_1^z \end{aligned}$$

In this form the coefficient contains the variable factor α^z, which is not to be allowed, for the coefficient must be kept constant if such an equation is to have any useful meaning, as we have seen, and hence in order to keep the coefficient constant the exponent must take a new value. This may be seen more easily from equation (18) which is arranged in a form convenient for computing the exponent from experimental data. B appears in the only term in the denominator while two of the terms of the numerator are independent of it, and hence to multiply B by a constant will change the computed values of z. This difficulty disappears when the exponent is constant. It is sometimes a convenience to be able to change the unit in which B is expressed, for example in shifting the decimal, or to use voltage or current instead of the flux, since they are usually proportional, and this is equivalent to a change of unit.

Another difficulty in computing the exponent from equation (18) for values of B approaching unity, is that small errors in the experimentally determined quantities introduce very large errors in the computed exponent. For points very near unity the equation fails entirely, as unity is an essential singular point of the function representing z, the denominator becoming zero. For all ordinary work this difficulty does not enter as only large values of B are used. In Figs. 20 and 21 the lowest value of B reached was 40. For the experimental determination at lower values recourse would have to be had to a null method such as that of Campbell[11] who has used a mutual inductance and vibration galvanometer.

On the whole, the determination of the actual exponent is of little practical importance. It is much more difficult to determine than the ratio of variation, it depends upon the unit in which the independent variable is expressed, and after it is once determined its use, as in interpolation, requires logarithms even for small intervals. The ratio of variation, that is, the slope of the logarithmic curve, is much more convenient to use in interpolating over small intervals. The fact that a constant exponent is the same as the ratio of variation has led to a failure to distinguish between them when the exponent is not constant, and this has introduced considerable confusion, not only in the literature of iron losses, but in the other fields in which the same ideas are made use of. Many attempts have been made to measure the variation of the exponent by methods which assume a constant exponent.

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[11] Proc. Phys. Soc. London, **22**, p. 207; 1910.

Recently Richter[12] has proposed a two-constant formula to supplant the classical form, using only the first power and the square of B so as to avoid fractional exponents. It is of the form

$$W = aB + cB^2$$

where a and c are constants. Jouaust[13] has commented favorably on it. It is easily seen that the ratio of variation for iron whose losses follow such a law can not be greater than 2. For differentiating and dividing by the original equation

$$\frac{dW}{W} = \frac{adB + 2cBdB}{aB + cB^2} = \frac{a + 2cB}{a + cB} \cdot \frac{dB}{B}$$

$$\frac{\frac{dW}{W}}{\frac{dB}{B}} = \frac{a + 2cB}{a + cB} \qquad (20)$$

and from its form the right member of this equation can not be less than 1, which it approaches for very small values of B, and it can not exceed 2, which it approaches for large values of B. It may also be seen from (20) that if we plot the ratio of variation against B the resulting curve slopes upward throughout and hence has neither maxima nor minimum, or more rigorously, since the left member is the ratio of variation we may get its slope by differentiating in regard to B.

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[12] Electrotechnische ZS., Dec. 8, 1910.

[13] Lumière Électrique, **18**, p. 241, 1911.

$$\frac{d}{dB}\left(\frac{\frac{dW}{W}}{\frac{dB}{B}}\right)=\frac{2c(a+cB)-c(a+2cB)}{(a+cB)^2}=\frac{ac}{(a+cB)^2}$$

Which shows the slope to be always positive as stated.

Although Richter's formula may be very useful when applied to the relatively narrow limits of flux density used in commercial transformer design, it will evidently not meet the requirements over such wide ranges as shown for transformers S_1 and S_8 in Figs. 20 to 23, or for such special cases as shown for transformer F in Figs. 18 and 24, where the ratio of variation passes through maxima and minima, has negative slopes, values greater than 2, etc. Moreover, as our present interest is chiefly in exponents and ratios of variation attaining values of 2 or greater, the formula will not suffice.

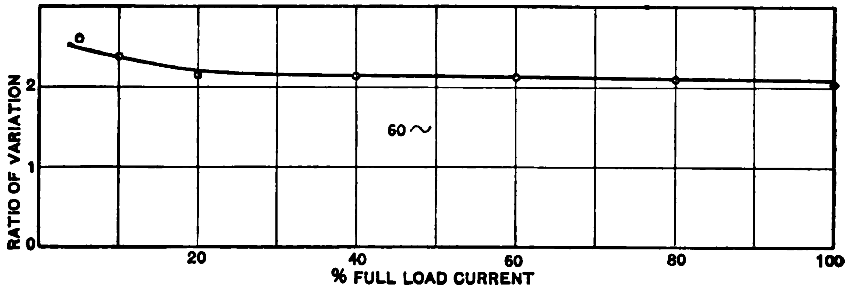

Fig. 24.—*Ratio of variation for transformer F at 60 cycles.*

6. THE SLOPE OF THE RATIO CURVE DETERMINED BY THE RATIO OF VARIATION

To return to the question of the ratio curve of the current transformer on noninductive load we had found, by means of equation (10) that if the Steinmetz exponent for the total iron losses could be taken as constant then the ratio would increase with increasing current for exponents greater than 2, and would decrease with increasing current for exponents less than 2, the latter being the type of curve almost universally met with. We were unable to compare this theory with experimental results as experiment showed that the exponent was not constant. This led to the foregoing investigation of the relation between the exponent and the ratio of variation, and of the methods used in their determination, and we may now find a more general condition which determines the slope of the transformer ratio curve.

The previous statement of the dependence of the slope of the ratio curve upon the value of a constant exponent holds in exactly the same way for the general case of a variable exponent if the ratio of variation be substituted for the exponent. In fact the development may be made without assuming any empirical relation between the flux and the total loss. By equation (5) the ratio

$$R = n + \frac{F}{I_2}$$

where n is the number of turns and F the core loss component of the exciting current. If W is the core loss, E_1, E_2 the primary and secondary voltages, and r_2 the secondary resistance then

$$F = \frac{W}{E_1} = \frac{nW}{E_2} = \frac{nW}{r_2 I_2} \qquad (21)$$

and the ratio becomes

$$R = n + \frac{nW}{r_2 I_2^2}$$

Differentiating,

$$\frac{dR}{dI} = \frac{n}{r_2} \cdot \frac{I_2 \dfrac{dW}{dI_2} - 2W}{I_2^3} = \frac{nW}{r_2 I_2^3} \left(\frac{\dfrac{dW}{W}}{\dfrac{dI_2}{I_2}} - 2 \right)$$

Replacing F from (21)

$$\frac{dR}{dI} = \frac{F}{I_2^2} \left(\frac{\dfrac{dW}{W}}{\dfrac{dI_2}{I_2}} - 2 \right) \qquad (22)$$

The fraction within the parentheses is the ratio of variation of the core loss with respect to the current, but since the current is proportional to the flux, this is the same as the ratio of variation with respect to the flux. Hence we may also write

$$\frac{dR}{dI}=\frac{F}{I_2^2}\left(\frac{\frac{dW}{W}}{\frac{dB}{B}}-2\right) \tag{23}$$

Either (22) or (23) shows that the ratio of a current transformer will rise with increasing current when the ratio of variation is greater than 2, and that it decreases with increasing current when the ratio of variation is less than 2. This latter is, as already stated, almost universally the case.

That the experimental results obtained from the measurements of transformer F verify this conclusion may be seen from a comparison of the ratio curves of Fig. 4, with the curves of the ratio of variation of Figs. 18 and 24. At 60 cycles the ratio curve slopes upward throughout its length and in agreement with this the ratio of variation is greater than 2 over the whole range. In the curve at 25 cycles the ratio increases to half load and then slowly decreases to full load while in agreement with this the ratio of variation is greater than 2 for low currents and less than 2 for the larger currents, passing through the value 2 at approximately half load.

To test equation (22) quantitatively Table III has been computed for this transformer from the quantities plotted in the figures referred to.

TABLE III

Slope of Ratio Curve in Percentage Change of Ratio per Ampere

Secondary current	60 cycles		25 cycles	
	Calculated	Observed	Calculated	Observed
1	+0.09	+0.09	+0.27	+0.09
2	+ .06	+ .04	+ .04	+ .04
2.5			.00	.00
3	+ .05	+ .03	− .02	− .02
4	+ .02	+ .02	− .07	− .05
5	+ .01	+ .01	− .09	− .07

With the exception of the 1 ampere point at 25 cycles the agreement is extremely satisfactory, the difference in the calculated and observed values of the ratio curve not exceeding 0.02 per cent for the ratio change per ampere. The discrepancy at the one point is due to the great difficulty in obtaining sufficiently accurate determinations of both the ratio and the core loss at the low loads. In fact the agreement at the 1 ampere 60 cycle point must be regarded as accidental. For currents less than an ampere the accuracy is not great enough to allow any comparison to be made, as is shown by plotted points in Fig. 4. This is not surprising when the magnitude of some of the quantities is considered. For example, at one ampere, 60 cycles, the core loss was but 0.003 watt and for many of the lower points the corrections for the energy taken by the measuring instruments was more than half the total quantity measured.

In Fig. 25 the loss and the ratio of variation for the core of a power transformer designated as transformer G, are plotted for low flux densities, the maximum value reached being 235 gausses. The ratio of variation decreases from slightly over 2 at low voltage to slightly less than 2 at the highest voltage shown. When tested as a current transformer it gave a very flat curve as would be predicted from theory, and actually passed through a maximum; but the change in ratio was only a very few hundredths of a per cent.

A few other cases have been found in which the ratio of variation was slightly greater than 2 at low flux densities, as, for example, with transformer S_2, discussed in connection with Fig. 19, but no other case has been found in which the phenomenon of the ratio of transformation increasing with the current was anywhere nearly as pronounced as with transformer F. Reference has already been made to the fact that occasionally a transformer had been found whose ratio curve showed a tendency to turn down instead of up at the extreme low current end of the curves, and although passed over at the time as possibly due to errors of measurement, it seems entirely probable that these transformers would have shown core loss curves whose ratios of variation reached values of 2 or more.

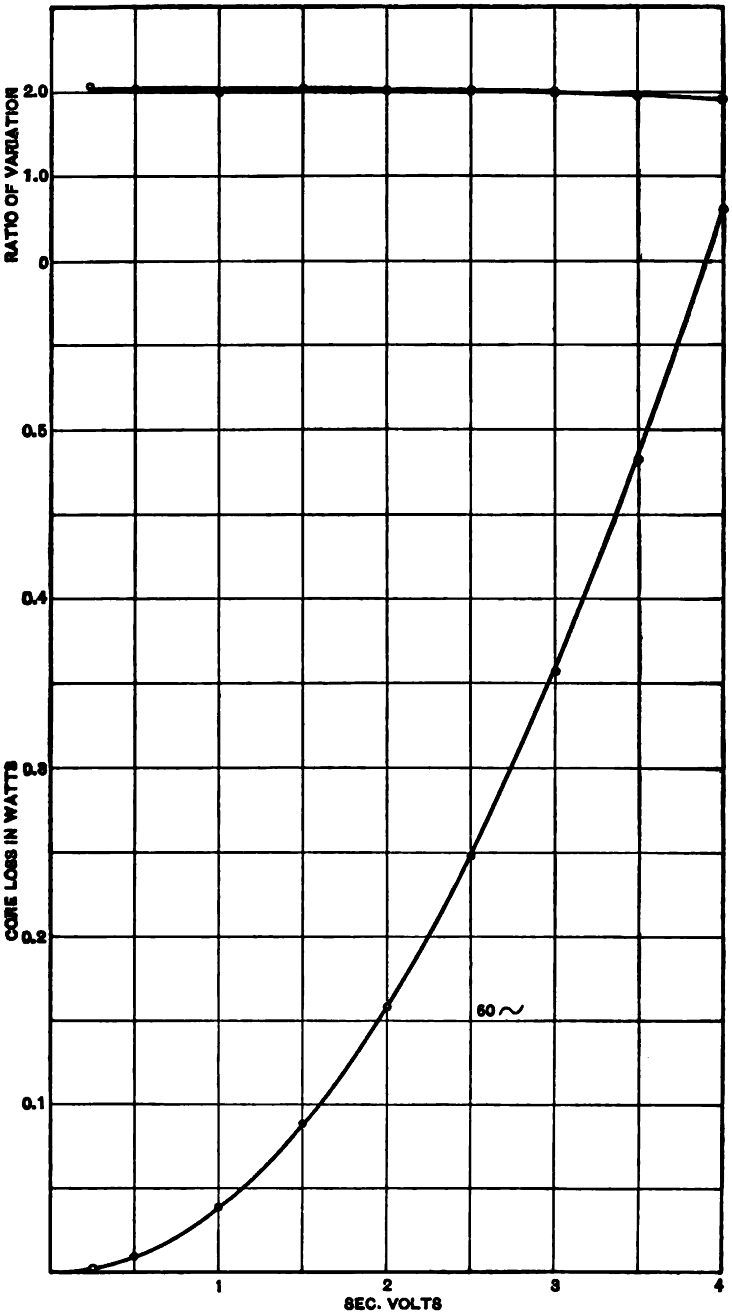

Fig. 25.—*Core loss and ratio of variation for tranformer G at 60 cycles. Maximum B=235.*

It might be supposed that all transformer iron might show high values of the ratio of variation if the measurements were pushed to low enough values of flux density. To determine this point recourse would have to be had to either very large masses of iron or to more sensitive methods, such as Campbell's, to which reference has already been made, for with some transformers the ratio of variation was well under 2 at the lowest flux densities that could be reached with the electrodynamometers used in these measurements. The large changes that magnetic history may introduce into the measured values of the permeability and the core loss at low densities where the effect is much greater is another disturbing factor in such measurements. It has been shown [14] that considerable errors may be introduced into ratio and phase angle measurements by the variations in the magnetic constants due to the magnetic history of the core.

In the case of transformer H in which the ratio could be varied by series-parallel grouping of the primary windings the determination of the ratio and phase angle was carried to extremely low values of the current, and yet the ratio curve showed no tendency to turn down, (Fig. 26); on the contrary, the upward curvature steadily increases, indicating that the ratio of variation is still below 2. By special manipulation the sensibility did not fall below 1/1500 even at 2.5 per cent of load. Incidentally these curves show how nearly the same form the ratio and phase angle curves may take. By changing the scale of one they would be nearly coincident.

Although there is need for a systematic study of iron losses at moderate and low flux densities, the data available being neither comprehensive nor systematic, at least nine other observers [15] have reported values of the Steinmetz exponent as great as or greater than 2. As in nearly every case increasing or decreasing values of the "exponent" are reported, the values may be interpreted as the ratio of variation.

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[14] For a detailed discussion, see Agnew and Fitch, this Bulletin, **6**, p. 297, 1909. Reprint 130.

[15] Rayleigh: Phil. Mag., **23**, p. 225; 1887. Ewing and Klassen: Phil. Trans. p. 985, 1893. Maurach: Ann. d. Phys., **311**, p. 580; 1901. Wild: Electrician, **56**, 705; 1906. Sumpner: Electrician, **56**, 768; 1906. Wilson, Winston, and O'Dell: Proc. Roy. Soc., **80**, p. 548; 1908. Lloyd and Fisher: Bull. Bur. Standards, **5**, p. 453; 1909. Reprint 109. Reed: Elec. Journal, **7**, p. 361; 1910. Wooldridge: Proc. Am. Inst. Elec. Eng., **30**, p. 139, Jan. 1911.

This dependence of the slope of the ratio curve upon the ratio of variation raises an interesting point in regard to methods sometimes used in the ratio determination. This method is to measure both primary and secondary currents separately by sensitive dynamometers, but as this requires the extra impedance of the dynamometer to be placed in the secondary circuit, the performance of the transformer is modified by this measuring instrument. Attempts have been made to correct for this by adding double the impedance so as to get a correction to apply in reducing the values to what would be obtained if the impedance of the instrument were not in circuit, or to reach the same end by determining the error thus introduced on a few transformers and thus to get a "blanket correction" to apply to all measurements. It is evident that this procedure may introduce considerable errors if the core should happen to have its ratio of variation pass through the value 2, and hence the ratio of transformation have a maximum. Accordingly, such a plan should not be used for the most accurate work, as it assumes precisely similar ratio of variation curves in all cases.

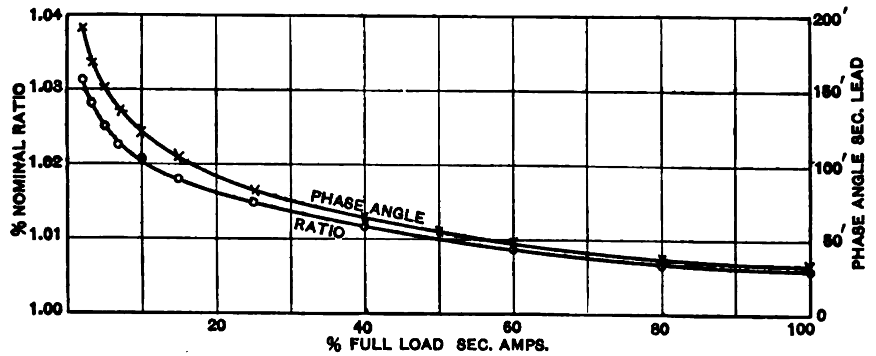

Fig. 26.—*Ratio and phase angle curves of transformer H.*

7. BEARING ON DESIGN

While the relation between the slope of the ratio curve and the ratio of variation has been established only for the case of noninductive load, it may be said that a transformer showing a good performance on noninductive load will usually give good ratio curves on inductive loads, and vice versa, so that while quantitatively the relation will not hold, it will do so in a general qualitative way. Evidently for a given total loss it would be better to select a grade of steel having a relatively high eddy current and low hysteresis loss, since the former would probably vary almost exactly as the square of the flux at the low densities used. Of course in this region the eddy current loss is usually less than the hysteresis loss, but experiments on different kinds of steel might result in finding one whose ratio of variation for the total iron losses would be nearly constant and have a value of approximately 2. It would, of course, be desirable to have such a property coupled with a high permeability so as to keep the phase angle small.

It would also seem to follow that for a given frequency and a given secondary impedance load, the ratio performance might be better in a transformer using relatively thicker sheets, so as to increase the eddy currents, or even by the use of an auxiliary winding to be closed through a resistance. But for general work, where different frequencies and reactance loads are to be used it would not be advantageous, since the amount of the departure from the ratio of turns would be increased, and hence the change in the ratio resulting from a change in frequency or in impedance load would also be increased, although the curve would be flatter for any given frequency and impedance load.

8. DISTORTION OF WAVE FORM

There has been a considerable amount of discussion as to whether wave distortion in a current transformer can introduce appreciable errors in measurements in which the ratio or phase angle of the transformer enters. Of course in a circuit containing iron there must theoretically be some distortion, however small, and a greatly exaggerated importance has often been assigned to it. Robinson has shown by means of the oscillograph that even in the case of a complicated wave form the distortion can not be important,[16] but no numerical determinations of the actual magnitude of the distortion have been published. A really satisfactory answer to such a question must depend upon quantitative data. Since, if distortion is allowed for, there are two possible definitions of the ratio of transformation and of the phase angle, and as there seemed to be a possibility of the same error entering into both the direct determinations of the constants of the transformer and in the determination of the exciting current components, it was thought advisable to attempt some quantitative determinations of the magnitude of the distortion. The question of the effect of possible distortion on ratio and phase angle has already been discussed.

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[16] Trans. Amer. Inst. Elec. Eng., **28**, p. 1005; 1909.

Two cases are to be distinguished, that of a sinusoidal primary current, and the much more complicated one in which the primary current is nonsinusoidal. In neither case, however, can the oscillograph or even the curve-tracer be made to give any but negative results, by merely analyzing the primary and secondary current waves separately. The amount of distortion is so minute that some indirect method must be employed.

The following method was used in the case of a sinusoidal primary current, taken from a star connected generator whose individual phases have very good waves. Two shunts R_1 and R_2 were placed in the primary and secondary, respectively, and the value of R_2 adjusted to give the same in-phase drop as I_1R_1 as in the method of getting ratio. (See Fig. 6.) All the distortions present in I_2R_2 will appear in Q. Hence, if we in some way determine the amount of distortion in Q, it will immediately give us the distortion in the secondary current. The advantage of this procedure is that the harmonics present will form a very much larger part of Q than of I_2R_2, and hence it is much like measuring a small difference directly rather than as the difference between the measurements of two large quantities. Small amounts of impurities in the primary wave will not appreciably affect the results.

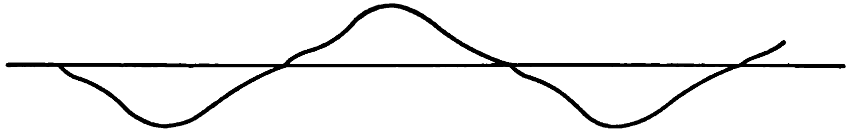

Fig. 27.—*Wave form of the quadrature component in the secondary current of transformer F, as determined by the Rosa curve tracer. 25 cycles, full load.*

In Fig. 27 is reproduced an example of the wave form of the complex emf Q, as determined by the Rosa curve-tracer. It was taken on transformer F at 25 cycles, 5 amperes secondary current. From an analysis of this wave by Thomson's method, the following data are computed for comparison with some of the data derived from the direct measurements of ratio, and of core loss and magnetizing current:

Effective value of 25 cycle component from curve	0.00496 volt
Effective value of 25 cycle component by dynamometer	0.00487 volt
Magnetizing current computed from curve	0.511 amp
Magnetizing current observed	0.500 amp
Percentage of third harmonic in curve	16.00 per cent
Percentage of fifth harmonic in curve	3.00 per cent
Percentage of third harmonic in secondary current	0.13 per cent
Percentage of fifth harmonic in secondary current	0.03 per cent
Distortion due to third harmonic in terms of effective values	1 part in 1 000 000
Distortion due to fifth harmonic in terms of effective values	1 part in 20 000 000

The accuracy of the experimental data was not great enough to allow more than two harmonics to be computed, as the difficulties of tracing a wave of so small an emf are considerable. In fact, the close agreement shown must be in part accidental. In order to trace a wave the emf of which was only 5 millivolts, it was necessary to use a high sensibility galvanometer, to place extra wide contact pieces on the rotating contact maker, and to use various other precautions.

A direct analysis of the emf *Q* was carried out by des Coudres' direct dynamometer method,[17] in which the emf to be analyzed is applied to the moving coil of a dynamometer while a current from a machine giving any desired harmonic is passed through the fixed coil. The resulting deflection is due entirely to this particular harmonic. In order to obviate the difficulty of phase relations, the machines were run just out of synchronism, giving a continuous phase shift. The dynamometer would then deflect back and forth, following the continuously changing phase relation, the maximum travel either side of the zero giving a measure of the emf of the harmonic that was being determined. For the third harmonic the dynameter made three complete swings for one cycle of the synchronizing lamp, for the fifth, five, and so on. Only two harmonics could be determined in this way, on account of experimental difficulties, the chief of which was due to the inertia of the moving coil of the dynamometer, causing it to have an appreciable period of its own. For this reason the machines had to be run almost exactly in synchronism so that the changes in deflection would be slow. The deflections which it was possible to obtain were only a few millimeters.

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[17] des Coudres, Electrotechnische ZS., **21**; pp. 752 and 770; 1900.

The distortion found for a modern, high grade current transformer under various conditions of frequency, impedance load, and current is given in Table IV.

TABLE IV

Distortion Introduced by Transformer *J*. Primary Current Sinusoidal

Frequency	Impedance in sec.	Sec. current	Per cent third harmonic	Per cent fifth harmonic
25	1 ammeter	1	0.11	0.03
25	1 ammeter	2	.08	.03
25	1 ammeter	3	.08	.03
25	1 ammeter	4	.08	.03
25	1 ammeter	5	.08	.03
25	1.6 ⌒	1	.31	.09
25	1.6 ⌒	2	.33	.06
25	1.6 ⌒	3	.34	.07
25	1.6 ⌒	4	.34	.07
25	1.6 ⌒	5	.36	.08
25	1 ⌒+8 mh	1	.27	.01
25	1 ⌒+8 mh	2	.26	.01
25	1 ⌒+8 mh	3	.27	.02
25	1 ⌒+8 mh	4	.28	.03
25	1 ⌒+8 mh	5	.28	.05
60	1 ammeter	1	.06	.02
60	1 ammeter	2	.05	.03
60	1 ammeter	3	.04	.02
60	1 ammeter	4	.04	.02
60	1 ammeter	5	.03	.02
60	1.6 ⌒	1	.15	.06
60	1.6 ⌒	2	.16	.04
60	1.6 ⌒	3	.16	.04
60	1.6 ⌒	4	.14	.04
60	1.6 ⌒	5	.14	.04
60	1 ⌒+8 mh	1	.19	.03
60	1 ⌒+8 mh	2	.20	.03
60	1 ⌒+8 mh	3	.22	.03
60	1 ⌒+8 mh	4	.22	.04
60	1 ⌒+8 mh	5	.22	.04

The percentage of harmonic present in each case is seen to be independent of the current, so far as the accuracy of the method is concerned. Evidently the amount of distortion in a current transformer is extremely small, for a sinusoidal primary wave the highest figure obtained, and that under severe conditions, being but 0.36 per cent of the fundamental, and this adds less than one part in one hundred thousand to the effective value. About the same value is obtained for the 25 cycle, low impedance load as was obtained under similar conditions for transformer F, which was the transformer showing the peculiar ratio curves. In no case is the amount of fifth harmonic introduced great enough to change the ratio of effective values by as much as one part in a million.

In order to determine the distortion for the case of a non-sinusoidal primary wave the method was considerably modified. For the experiment two transformers having 5 to 5 ampere windings were chosen in order that precisely similar shunts might be used in primary and secondary, thus eliminating errors due to difference in the inductances of the shunts. The most essential modification of the method consisted in reducing the *measured value* of the quadrature resultant electromotive force Q (Fig. 6) to zero, by introducing a variable self inductance in the secondary so as to vary the phase angle of the transformer, in fact to bring it to zero. Under this condition if there were no distortion introduced by the transformer there would be no resultant emf whatever to be applied to the moving coil of the dynamometer, and hence any resultant that is found in Q is due to distortion within the transformer. The diagram of connections is shown in Fig. 28. For convenience a dynamometer having 2 separate field coils for 1 and 5 amperes was used but two separate instruments would have done as well. The self-inductance of the moving coil was compensated and the coil set at the position of zero mutual inductance. Two motor-driven 2-phase alternators rigid on the same shaft and designed for 25 and 75 cycles were used as sources. The 5-ampere coil of the dynamometer could be thrown in or out of the primary circuit by the switch M, while the 1-ampere coil could be connected to either phase of the 75-cycle machine.

The procedure was to throw M to the right, N up, and adjust R_2 for the ratio, S being open. Then throw M left, N down, and adjust the self-inductance L for no deflection or Q. To get both adjustments it was necessary to successively approximate, and it was found convenient also to change the frequency. The primary current was maintained constant at full load by the ammeter A_1. When these adjustments were made, with M left, N up, S was thrown first left and the in-phase component of the distorted emf read on the upper dynamometer. S was then thrown right and the quadrature component measured. S connects the moving coil to the source of the third harmonic. The results which were obtained at a frequency of 38 cycles, are shown in Table V.

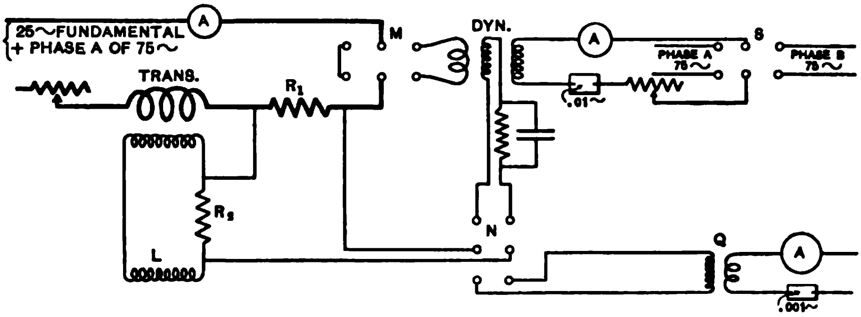

Fig. 28.—*Connections for measuring the distortion in a current transformer with a nonsinusinusoidal primary wave.*

TABLE V

Distortion emf (volts)

Transformer	Wave form	In phase	In quadrature	Total	Change in effective value
K	20% dimple	0.00050	0.00017	0.00053	1 in 4000
"	20% peak	21	51	55	1 in 10000
S_1	20% dimple	77	28	82	1 in 2500
"	20% peak	32	33	46	1 in 6000

In computing the change in the effective value only the in-phase component of the distortion emf was taken into account as the effect of the quadrature component would be entirely inappreciable. The current was 5 amperes, and R_1 and R_2 approximately 0.075 ohm.

Transformer K was of an old type showing a poor ratio curve, and S_1 was a special transformer.

We may conclude from the results of these determinations of the magnitudes of the distortion introduced by current transformers, that the distortion is so small that it is of theoretical interest only, amounting as it does to less than one part in one hundred thousand in effective value when the primary current is sinusoidal, and to but one part in two thousand five hundred in the most unfavorable case, and that with 20 per cent of third harmonic in the primary wave. When we consider the good wave forms given by modern alternators, we may safely say that in no practical case can the distortion be detected by its introducing errors into the measurement of either emf, current or power, even with the most accurate instruments available.

It also follows that there is no appreciable difference in the ratio of transformation whether it be defined as the ratio of the mean effective values of the currents, or as the ratio of the primary to the undistorted part of the secondary; and hence there can be no objection against any of the null methods now in use, whether the detector be an electrodynamometer, an electrometer, or a rotating commutator with a direct-current galvanometer.

9. EFFECT OF WAVE FORM UPON RATIO AND PHASE ANGLE

While, as we have seen, no appreciable distortion is introduced by the transformer, the wave form may change the ratio appreciably. This has been pointed out by Rosa and Lloyd,[18] who made some measurements, the result of which showed that while small, the effect could be detected by the methods then in use, if the distortion was large.

In Fig. 29 are plotted the results of measurements of the ratio of transformer J, which is a high-grade instrument, with 5 different wave forms, and with 2 different secondary impedance loads. It should be noted that the vertical scale is greatly magnified so as to separate the curves, also that the impedance load for the upper curves is somewhat severe. The curves are very nearly parallel, and the ratio at the smaller impedance load even with a wave distorted by 20 per cent of third harmonic differs only 0.05 per cent either way from the value with a sine curve, while with the large impedance in the secondary the corresponding change is only 0.15 per cent and these are only half as great at 10 per cent distortion. At 60 cycles the corresponding figures would be considerably less. The relative accuracy of the measurements was 0.02 per cent.

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[18] This Bulletin, 6, p. 30; 1909.

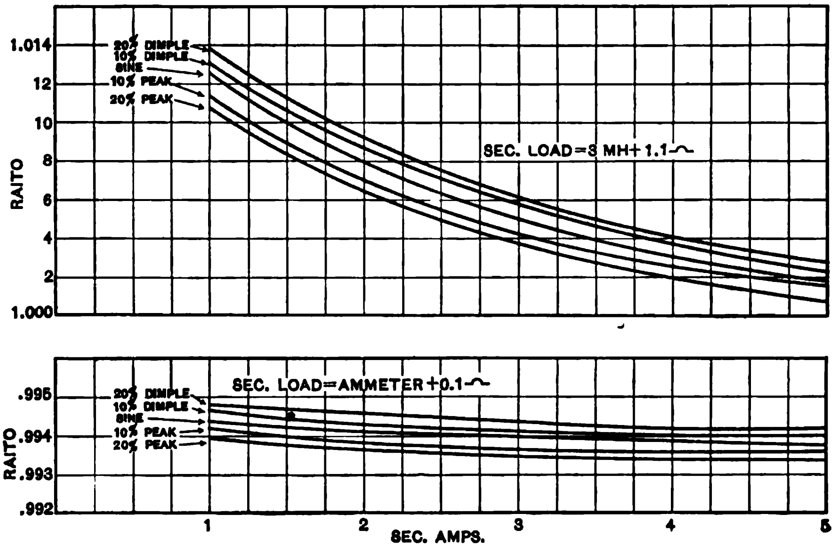

Fig. 29.—*Effect of wave form upon ratio. Transformer J, 25 cycles.*

The dimpled wave raises the ratio and the peak wave lowers it, which is in the direction that theory would predict, since a dimpled wave increases the iron losses and a peaked wave decreases them for the same effective value of emf, as has been shown by Lloyd [19] and others.

The effect of wave form on the phase angle is very small. For example with 25 cycles, 1.1 ohm resistance in the secondary circuit, full load current, the following values of the phase angle were determined.

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[19] This Bulletin, 5, p. 381, 1909, Reprint No. 106.

Wave form	Phase angle
20% peak	33.8′
sine	35.0′
20% dimple	35.6′

About the same differences persisted over the current range, as near as could be told; that is, half a minute to a minute. The sensibility was proportionately less at the lower currents. Again, the direction of the change found is the same as would be predicted from theory. It is too small to be of any practical significance. With 10 per cent distortion the effect was too small to be detected with certainty.

The effect of wave form upon ratio and phase angle is very similar to that of small changes in frequency, as might well be expected, and with good transformers is entirely negligible for the wave forms met in practice.

10. SUMMARY

1. While the ratio of transformation of current transformers usually decreases with increasing current, it may increase in individual cases, or even pass through a maximum.
2. The ratio and the phase angle performance may be accurately computed from the magnetic data of the core.
3. In general the slope of the ratio curve may be qualitatively predicted from the value of the Steinmetz exponent if the latter be assumed to be constant. But the iron losses, particularly at the low flux densities used, depart too widely from such a simple law for accurate work.
4. The slope of the ratio curve may be accurately computed from the slope of the curve obtained by plotting the core loss against the flux on logarithmic coordinate paper.
5. It is proposed that this logarithmic slope, or logarithmic derivative shall be called the *ratio of variation*. It is much more useful than the actual exponent.

6. The methods now in use for determining the "exponent" fail to give a true exponent that will satisfy the equation $W = KB^z$, unless z is a constant. The quantity actually determined by these methods is the ratio of variation.

7. The wave form of the secondary of a current transformer may be considered to be the same as that of the primary current for even the most precise measurements, as the distortion within the transformer is entirely negligible.

8. While the effect of variations in wave form on ratio and phase angle may be detected by accurate measurements, it is too small to be of practical importance, being of the same order of magnitude as the effect of small changes in frequency.

9. The null methods used for accurate determinations of ratio and phase angle all give the theoretically correct results, well within the experimental error, so that the accuracy attainable is decidedly greater than is required in practice.

11. BIBLIOGRAPHY

The following list is not intended as a complete bibliography of the current transformer, but it is believed that all the more important papers are included:

1. Campbell, A.: On the measurement of very large and very small alternating currents.
Phil. Mag., **52**, 271; 1896.
2. Schrottke, F.: Ueber Drehfeldmessgeräthe.
Elektrotechnische Zeitschrift, **22**, p. 657; 1901. (Current transformers are discussed on p. 665.)
3. Wilder, E. L.: Operation of the series transformer.
Elec. Journal, **1**, p. 451; 1904.
4. Curtis, K. L.: The current transformer.
Proc. Amer. Inst. Elec. Eng., **25**, p. 715; 1906.
5. Drysdale, C. V.: Some measurements on phase displacements in resistances and transformers.
Electrician, pp. 726 and 783; 1906.
6. Makower, A. J.: Measurement of phase difference.
Electrician, **58**, p. 695; 1907.
7. Harrar, E. S.: The series transformer.
Elec. World, **51**, p. 1044; 1908.
8. Drysdale, C. V.: The use of shunts and transformers with alternating current measuring instruments.
Phil. Mag., **21**, p. 136; 1908.
9. Edgcumbe, K.: Industrial measuring instruments, p. 134.
New York; 1908. (D. Van Nostrand Co.)

10. Lloyd, M. G.: What is the ratio of a transformer?
Elec. World, **52**, p. 77; 1908.

11. Rosa, E. B. and M. G. Lloyd: The determination of the ratio of transformation and of the phase relations in transformers.
Bull. Bur. Standards, **6**, p. 1; 1909.

12. Agnew, P. G. and T. T. Fitch: The determination of the constants of instrument transformers.
Bull. Bur. Standards, **6**, p. 281; 1909, Reprint No. 130.
Elec. World, **54**, p. 1042; 1909.

13. Orlich, E.: Über die Anwendung des Quadranten-electrometers zu Wechselstrommessungen.
Electrotechnische Zeitschrift, **30**, pp. 435, 466; 1909. (A discussion of the measurement of the constants of the current transformer is given on p. 468.)

14. Robinson, L. T.: Electrical measurements on circuits requiring current and potential transformers.
Trans. Amer. Inst. Elec. Eng., **28**, p. 1005; 1909. (Discussion, p. 1040.)

15. Tobey, H. W.: Recent developments in transforming apparatus.
Electrician, **63**, p. 659; 1909.

16. Wernicke, G.: Elektrotechnische Messungen und Messinstrumente, p. 59.
Braunschweig; 1909. (Vieweg u. Sohn.)

17. Sterzel, K. A.: Stromwandler fur Wechselstrom-Leistungsmessungen.
Electrotechnische Zeitschrift, **30**, p. 489; 1909.

18. Genkin, W.: Sur les transformateurs d'intensité.
Lumière Électrique, 8, p. 67; 1909.

19. Young, A. P.: Theory and design of the current transformer.
Jour. Inst. E. E., **45**, p. 670; 1910.

20. Campbell, A.: On the use of mutual inductometers.
Proc. Phys. Soc. London, **22**, 207; 1910. (Section on tests of current transformers, p. 217.)

21. Barbagelata, A.: Prova indiretta dei transformatori di misura per forti intensità di correnti.
Atti Assoc. Elettr. Ital., **14**, 639; 1910.

22. Edgcumbe, K.: Notes on instrument transformers.
Elec. Rev. (Lond.), **67**, p. 163; 1910.

23. Laws, F. A.: Determination of the constants of instrument transformers.
Elec. World, **55**, p. 223; 1910.

24. Sharp, C. H. and Crawford, W. W.: Some recent developments in exact alternating current measurements.
Proc. Amer. Inst. Elec. Eng., **29**, p. 1207; 1910. (Current transformer ratios are treated on pp. 1211–1220.)

25. Baker, H. S.: Current-ratio and phase-angle test of series transformers.
Elec. World, **57**, p. 234; Jan. 26, 1911.

WASHINGTON, *April 6, 1911.*

THERMODYNAMICS OF CONCENTRATION CELLS

By Henry S. Carhart

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INTRODUCTION

The most general expression of the laws of thermodynamics for an isothermal process, of which the well-known equation of Helmholtz for the electromotive force of voltaic cells is a particular example, may be written in the form

$$A = H + T\frac{dA}{dT}.$$

H denotes the change in the internal energy of the system and A the maximum work or the change of free energy for a reversible physical or chemical process conducted isothermally.

If A for 1 gram equivalent of an ion is expressed in terms of electrical work as nFE (n the valence of the cation, F the number of coulombs transported through an electrolyte by a gram equivalent, and E the emf), the equation becomes that of Helmholtz, namely,

$$nFE = H + TnF\frac{dE}{dT}, \text{ or } E = \frac{H}{nF} + T\frac{dE}{dT}.$$

A number of distinct cases occur in the application of the general equation.

First. $dA/dT = 0$ at all temperatures. This case is an expression of the so-called Thomson principle as applied to voltaic cells, which makes $dE/dT = 0$. In fact, the Daniell cell, set up with saturated copper sulphate and very dilute zinc sulphate (specific gravity 1.04)[1] as the electrolytes, and the Weston cell without cadmium sulphate crystals, have electromotive forces very nearly independent of temperature. They may therefore be classed under this head.

Another case in point is the purely physical transformation of the potential energy of gravity into the energy of electric transfer. The Des Coudres' cell,[2] consisting of two mercury columns of different height, joined by a solution of mercurous nitrate, the longer column being retained in position by a porous diaphragm, is another illustration of case one. The measurement of the emf in this arrangement is not very satisfactory, but the results are of the same order of magnitude as the calculated values. A single example will suffice.

The difference between the measured heights of the columns was 141.1 cm. Then, when 1 gram equivalent (200 g) of mercurous mercury is transferred electrolytically from the one elevation to the other, the decrease in potential energy is $141.1 \times 200 \times 980 = 27\,655\,600$ ergs $= 2.76556$ joules. The corresponding emf is $\frac{2.76556}{96530} = 0.0000286$ volt; the measured value was 0.000030.

Second. H has a constant value. The general equation above gives $\frac{dA}{A-H} = \frac{dT}{T}$. By integration $\ln (A-H) = \ln T + \ln a = \ln aT$. Whence $A - H = aT$. Since a is the constant of integration, $A - H$ is proportional to the absolute temperature T and $dA/dT = a$. It appears, therefore, that when dA/dT or dE/dT is a constant, H is either zero or has a constant value. Illustrations will follow later.

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[1] Helmholtz: Sitzungsber, Ber. Akad., pp. 22–39; 1882.

[2] Wied. Ann., **46**, p. 292; 1892.

Third. $A = 0$, and $H = -T\, dA/dT$. This condition can obtain only at some definite point of temperature where A passes through a zero value. Examples are several cases of transition, such as $ZnSO_4.7\ H_2O$ into $ZnSO_4.6\ H_2O$ at 39°, and white tin into gray tin at 20°. At the transition temperature the two phases are in equilibrium, like water and ice at 0°, and there is no free energy. But at the transition point dA/dT may be large, and $H = -T\, dA/dT$.

Fourth. As a fourth case we may include Nernst's recent modification of the general equation. Nernst[3] assumes the following empirical expressions for A and H in terms of the integral powers of the absolute temperature:

$$A = A_0 + a'T + b'T^2 + c'T^3 +$$
$$H = H_0 + aT + bT^2 + cT^3 +$$

From the general thermodynamic equation, when $T = 0$, $A_0 = H_0$; hence

$$\frac{A-H}{T} = \frac{dA}{dT} = (a'-a) + (b'-b)T + (c'-c)T^2 = a' + 2b'T + 3c'T^2.$$

Whence $a' = a' - a$, or $a = 0$; $2b' = b' - b$, or $b' = -b$; $3c' = c' - c$, or $c' = -\tfrac{1}{2}c$.

Finally, then,

$$A = A_0 + a'T - bT^2 - \tfrac{1}{2}cT^3 -$$
$$H = H_0 + bT^2 + cT^3 +$$

Since the same constants now appear in both equations, the a' may be replaced by a.

When the constants b and c are zero, the expression for A reduces to the simpler one containing only the first power of T, $A - H = aT$, and $dA/dT = a$, a constant as in case two, or the relation between A and T is a linear one.

Nernst assumes without sufficient justification that both $\frac{dA}{dT}$ and $\frac{dH}{dT}$ are zero when T is zero. The equations above show that $\frac{dA}{dT} = a$ when $T = 0$; hence the term aT in the expansion for A is not zero as Nernst has it. If it were zero, the expression for A would exclude the case of concentration cells, in which A

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[3] Thermodynamics and Chemistry, Sitzungsber. Berl. Akad.; 1909.

is proportional to the absolute temperature (for very dilute solutions), or is equal to a constant H plus a term proportional to the first power of the absolute temperature.

The same conclusion may be reached by a different demonstration, assuming only the one expansion,

$$H = H_0 + aT + bT^2 + cT^3 +$$

The general equation $A = H + T\frac{dA}{dT}$ gives $AdT - TdA = HdT$, or $\frac{TdA - AdT}{T^2} = -\frac{H}{T^2}dT$. Integrating,

$$\frac{A}{T} = \frac{H_0}{T} + a' - a \ln T - bT - \tfrac{1}{2}cT^2, \text{ or } A = H_0 + a'T - aT \ln T - bT^2 - \tfrac{1}{2}cT^3.$$

Then $$\frac{dA}{dT} = a' - a \ln T - a - 2bT - \frac{3}{2}cT^2.$$

If now this expression for A is generally true, it must be true when dA/dT is a constant. But in case two it was shown that dA/dT is a constant when dH/dT is zero for $T = 0$, as in the last solution. Hence a in the expressions above for both A and H is zero, and the two reduce as before to

$$A = A_0 + a'T - bT^2 - \tfrac{1}{2}cT^3 -$$
$$H = H_0 + bT^2 + cT^3 +$$

The reader will note that these demonstrations show only that while the coefficient of T in the expansion for H is always zero, it is not necessarily zero in the expansion for A.

THE EVIDENCE OF EXPERIMENT

It would appear antecedently probable that a concentration cell such as *Zn amal. conc.* | *$ZnSO_4$ solution* | *Zn amal. dil.* (where the dilute amalgam at least must be of a lower concentration than that corresponding to a saturated or two-phase condition) should have constant heat of dilution for the two amalgams; or, in other words, H should be constant. This proves to be true, for the emf as a function of the temperature is linear.

For two amalgams with a concentration ratio by weight equal to two, the per cent of zinc in the more concentrated amalgam being approximately 1.2, the equation representing the emf was found to be

$$E = -0.001455 + 0.00003084\ T.$$

For the centigrade scale this is equivalent to

$$E_t = 0.006964(1 + 0.00443\ t).$$

The constant 0.00443 is the temperature coefficient $\frac{1}{E_0}\frac{dE}{dT}$. It is much larger than the temperature coefficient of a perfect gas.

In the following table are the observed values of the emf compared with those computed by the first equation:

Temp.	Obs. emf	Comp. emf	Per cent difference
11°.1	0.007300	0.007307	+0.10
15°.4	7444	7439	− .07
19°.8	7574	7575	+ .01
24°.6	7720	7723	+ .04
29°.4	7870	7871	+ .01
32°.8	7983	7976	− .09
36°.6	8086	8094	+ .10
42°.0	8262	8259	− .04
47°.0	8417	8414	− .04

The greatest difference between the observed and the computed values is 0.008 millivolt. The experimental cell was placed in a large water bath with double walls, and a stirrer driven by an electric motor was used to insure equal temperatures of the two legs of the cell. The emf was measured by a Wolff's potentiometer and a Weston Normal cell.

The cell was then taken apart, the amalgams washed, and the cell was again assembled with a concentrated solution of $ZnCl_2$ as the electrolyte. The observations are best represented by the same linear equation as the one applying to the $ZnSO_4$. Both the heat of dilution of the amalgams and the temperature coefficient, therefore, remain unchanged when the anion Cl replaces the anion SO_4. The observed and computed values are compared in the table.

Temp.	Obs. emf	Comp. emf	Per cent difference
10°.1	0.007275	0.007276	+0.01
14°.9	7424	7424	.00
19°.6	7567	7569	+ .03
25°.3	7733	7744	+ .14
32°.1	7943	7954	+ .14
37°.3	8106	8114	+ .10
41°.8	8256	8253	− .04
47°.9	8460	8441	− .22
49°.3	8486	8485	− .01

In the diagram Fig. 1 the circles denote the observations for $ZnSO_4$ and the crosses those for $ZnCl_2$.

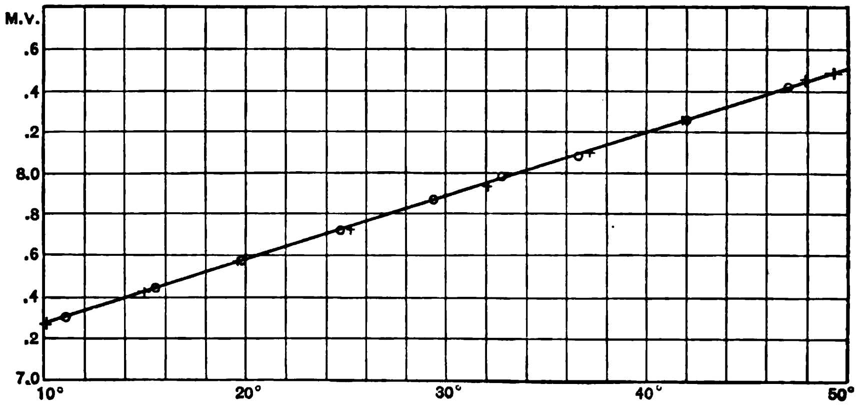

Fig. 1

Since the equation representing the emf is linear, it follows that dE/dT is a constant. The constancy of dE/dT may be shown in another manner. From the Helmholtz equation and the constant of the last equation, $\frac{dE}{dT}=\frac{E+0.001455}{T}$.

Then for 11°.1, $\frac{dE}{dT}=\frac{0.007300+0.001455}{248.1}=0.00003082$

15°.4		3085
19°.8		3083
24°.6		3083
29°.4		3083
32°.8		3086
36°.6		3082
42°.0		3085
47°.0		3085
	Mean	0.00003084

Cady[4] measured the emf of a sodium amalgam cell with the amalgams in a solution of *NaI* in pyridin. He assumed the correctness of the formula in the Nernst form for the emf of the cell as 0.0002 $T \log \frac{c_1}{c_2}$, in which the ratio of the concentrations replaces that of the osmotic pressures of the sodium in the amalgams. From his data the following values have been calculated:

For 4°, $\frac{dE}{dT}=\frac{0.0648-0.03}{277}=0.0001256$

7°		1264
9°		1262
19°		1260
22°		1264
	Mean	0.0001261

The constant 0.03 was the difference between the observed electromotive forces and those calculated from the Nernst formula. This constant is evidently too large. Calculating it by the Helmholtz equation for 7°, for example, it is 0.0265. Then, substituting this in place of 0.03 in the equation for dE/dT, the resulting value is 0.0001384. Again correcting the heat of dilution by this new approximate value of dE/dT, the emf due to the heat of dilution comes out 0.02665. The substitution of this value in place of 0.03 in the Helmholtz equation to determine dE/dT gives as the mean value 0.0001381. This is materially larger than Cady's value from the same data.

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[4] J. Phys. Chem., 2; 1898.

The equation for the emf is accordingly

$$E = 0.02665 + 0.0001381\ T.$$

The observed and computed values are the following:

Temp.	Obs. emf	Comp. emf	Per cent difference
4°	0.0648	0.06480	0.0
7°	654	6532	−.12
9°	656	6559	−.02
19°	668	6698	+.25
22°	673	6729	−.02

The heat of dilution of the sodium amalgam with mercury, computed from the equation for E, is 612.9 calories per gram molecule.

The following examples have been calculated from data given by Richards (Carnegie Institution of Washington, Publication No. 118):

Thallium, per cent of metal in the denser amalgam, 0.41.

$$\text{For}\ 0°, \frac{dE}{dT} = \frac{0.031543 - 0.001813}{273} = 0.0001089$$

$$15° \qquad \frac{0.033166 - 0.001813}{283} = 0.0001089$$

$$30° \qquad \frac{0.034810 - 0.001813}{303} = 0.0001089$$

Thallium, per cent of metal in denser amalgam, 0.111.

$$\text{For}\ 0°, \frac{dE}{dT} = \frac{0.016360 - 0.000436}{273} = 0.00005833$$

$$15° \qquad \frac{0.017238 - 0.000436}{288} = 0.00005833$$

$$30° \qquad \frac{0.018110 - 0.000436}{303} = 0.00005833$$

The linear equations for these two cases are:

$$E = 0.001813 + 0.0001089\ T.$$

$$E = 0.000436 + 0.00005833\ T.$$

The heat of dilution and the temperature coefficient are constant in both cases; both therefore negative the hypothesis of Nernst that the coefficient of T in the expression for A (or E) is zero. The relation between the emf and the temperature in all these amalgams is a purely linear one. The range of temperatures must be restricted to limits within which there is no change of phase in the materials composing the cell.

In addition to the cell with zinc amalgams the writer finds also that a concentration cell composed of cadmium amalgams and cadmium sulphate has an emf following the linear relation. The two amalgams had concentrations of approximately 2 per cent and 0.783 per cent. The following are the measured emf's compared with those computed by the equation

$$E = -0.000219 + 0.00003915\ T:$$

Temp.	Obs. emf	Comp. emf	Per cent difference
10°.05	0.010862	0.010862	0.0
15°.10	11063	11060	− .03
18°.42	11190	11190	.0
22°.10	11336	11334	− .02
26°.80	11517	11518	+ .01
33°.40	11773	11776	+ .03
38°.00	11942	11956	+ .12
43°.20	12160	12160	0.0

The heat of dilution comes out a small negative quantity of −10 calories per gram molecule of cadmium. The observations are plotted in Fig. 2, the straight line representing the equation for E.

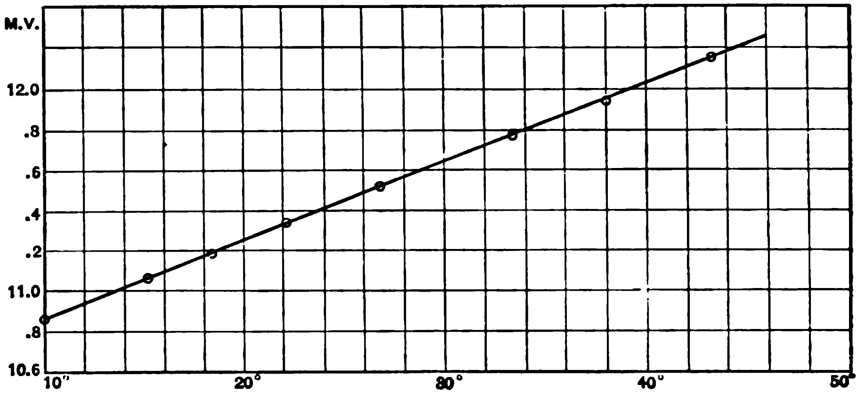

Fig. 2

THE SECOND TERM OF THE HELMHOLTZ EQUATION

The term $T\,dE/dT$, in cases where there is no change of phase in the materials, is a purely electrolytic thermoelectromotive force, which is very approximately linear. To illustrate this feature as applied to concentration cells, two amalgams were made by weighing out masses of mercury as one to two and depositing in them electrically the same quantity of zinc. The weight of zinc deposited was 0.6 and 1.2 per cent, respectively, of the weight of mercury. The concentration cell set up with these amalgams and a dense solution of zinc sulphate gave the following electromotive forces at the temperatures indicated:

Temp.	Obs. emf	Comp. emf
10°.70	0.007320	0.007319
14°.13	7420	7420
19°.62	7572	7581
24°.20	7713	7716
26°.25	7785	7776
31°.60	7940	7933
36°.80	8086	8086
39°.00	8146	8151

Equation: $E = -0.001022 + 0.0000294\,T.$

The corresponding heat of dilution of the two amalgams is -47 calories per gram molecule.

To measure the electrolytic thermoelectromotive force of the two amalgams, the two legs of the H-form of cell, identical in every respect as far as possible, were immersed in baths, one containing mixed ice and water, and the other water, the temperature of which was varied. The entire cell, except the short portion connecting the side tubes, was immersed. The results are the following:

Thermoelectromotive Force for the More Dilute Amalgam

Temp.	Obs. emf	Comp. emf
10°.30	0.01077	0.01077
15°.40	1611	1611
20°.47	2140	2141
25°.60	2676	2678
31°.10	3251	3253
36°.80	3852	3849
40°.20	4214	4205

Equation: $E_1 = 0.001046\,t.$

Thermoelectromotive Force for the More Concentrated Amalgam

Temp.	Obs. emf	Comp. emf
9°.41	0.00956	0.00957
14°.75	1496	1500
19°.65	1996	1998
25°.05	2542	2547
30°.60	3110	3112
35°.20	3582	3580
39°.30	4000	3993

Equation: $E_2 = 0.001017\,t.$

Then $\frac{dE}{dT} = \frac{E_1 - E_2}{t} = 0.001046 - 0.001017 = 0.0000290.$

Compare this with the value measured directly, namely, 0.0000294. The three tables are plotted in Fig. 3, with the scale for E on the left, and that for E_1 and E_2 on the right.

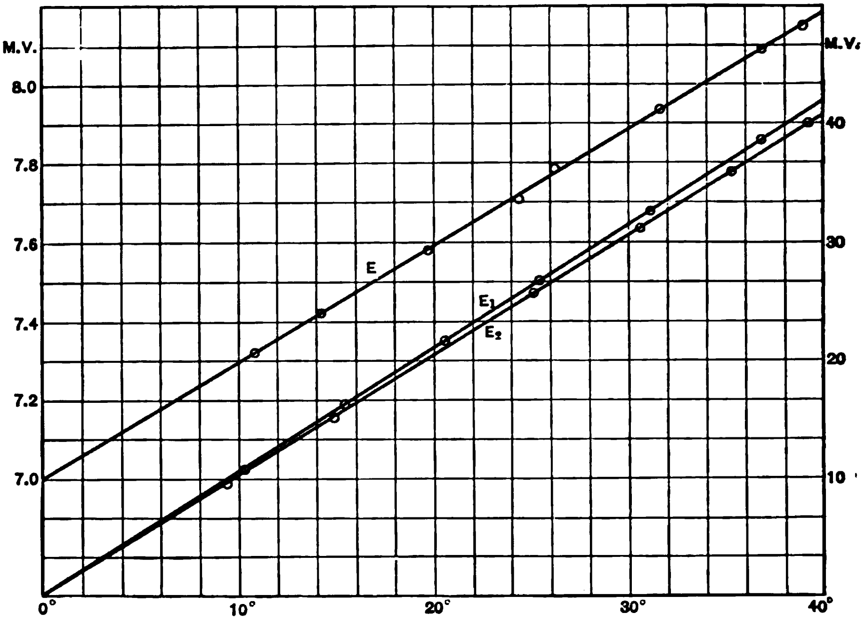

Fig. 3

The thermoelectromotive force is directed from the solution to the amalgam, and it increases as the *dilution* of the amalgam increases. In other words, the electrolytic thermoelectromotive force is a function of the concentration as well as of the temperature. Hence, the resulting emf of the cell is in favor of the dilute amalgam, which is thus the cathode of the cell. If the heat of dilution is positive, the emf derived from it is in the same direction as the emf resulting from the two thermoelectromotive forces; if the heat of dilution is negative, the corresponding emf is opposed.

The passage of a current through a concentration cell not only reduces the difference in concentration of the amalgam electrodes, but it tends to produce a temperature difference between them. At the anode the current encounters a back emf and heat is generated; at the cathode the thermoelectromotive force has the same direction as the current, and heat is absorbed. When the difference in concentration is entirely in the amalgam electrodes, the heat absorbed is greater than the heat generated, and such a cell converts its own heat and that of the surroundings into the energy of the electric current. It can not do so continuously, because its current reduces the difference of concentration on which the emf depends.

When the difference in concentration is in the electrolyte surrounding the electrodes, cases occur of positive heat of dilution and a negative temperature coefficient. An example is the following:

$$Zn \mid ZnCl_2.18.8\ H_2O \mid ZnCl_2.180\ H_2O \mid Zn$$

The quantity dE/dT for this cell[6] is -0.0000973; the heat of dilution is 4530 calories per gram molecule (Thomsen). The computed emf would be—

$$\text{emf due to heat of dilution,}\quad \frac{4530}{2\times 23040} = 0.09831$$

$$\text{emf at } 25^\circ \text{ equal to } T\frac{dE}{dT} = -298\times 0.0000973 = -0.02900$$

$$E = 0.06931$$

The mean observed emf at 25° was 0.06719 volt.

This concentration cell is precisely like a voltaic cell with a negative temperature coefficient. Its energy is derived from the heat of dilution, and it is difficult to see how the Nernst formula for the emf of a concentration cell can have any application whatever to it.

Since the relation between the thermoelectromotive forces of the above amalgams and the temperature is a linear one, the potential difference at the liquid-amalgam junctions may be computed from the expression TdE/dT. Thus, the potential difference between the zinc sulphate solution and the dilute amalgam (0.6 per cent) at 27° is

$$0.001046\times 300 = 0.3138 \text{ volt.}$$

For the concentrated amalgam (1.2 per cent) it is

$$0.001017\times 300 = 0.3051 \text{ volt.}$$

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[6] Phys. Rev., **29**, p. 329; 1909.

Then the emf of the concentration cell composed of the two amalgams and the zinc sulphate as electrolyte, owing to the thermoelectromotive forces at 27°, is

$$0.3138 - 0.3051 = 0.0087 \text{ volt.}$$

But there is a loss on account of the negative heat of dilution equal to about 0.001 volt. Hence

$$E = 0.0087 - 0.0010 = 0.0077 \text{ volt.}$$

The measured value was 0.0078 volt.

A COMPOSITE CONCENTRATION CELL

A concentration cell, in which the difference in concentration is entirely in the two electrolytes bathing the electrodes, may be combined with one in which the concentration difference is in the amalgam electrodes in such a manner that the complete cell may have zero temperature coefficient, and thus come under case one of the general equation.

For example, the cell

$$Zn\ amal. \mid ZnSO_4.50\ H_2O \mid ZnSO_4.190\ H_2O \mid Zn\ amal.$$

has an emf represented approximately by the equation

$$E_2 = 0.001527 + 0.00003084\ T.$$

The positive is the electrode in the more concentrated solution. If this cell be combined with the one whose equation was found to be

$$E_1 = -0.001455 + 0.00003084\ T$$

with the dilute solution in contact with the dilute zinc amalgam, the resulting emf of the combination will be the difference between the two equations representing the two components of the composite cell. Then

$$\begin{aligned} E_2 &= +0.001527 + 0.00003084\ T \\ \underline{E_1} &= \underline{-0.001455 + 0.00003084\ T} \\ E &= \quad 0.002982 + 0.0 \end{aligned}$$

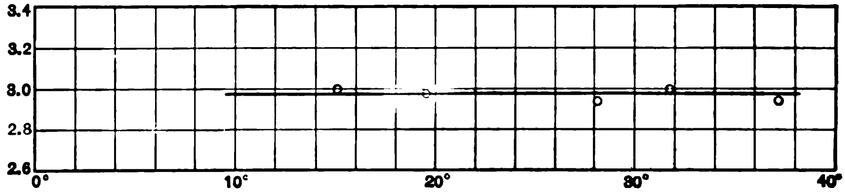

Fig. 4

The results of a single trial of such a cell are shown in Fig. 4. The amalgams were the same as those used in getting the data for Fig. 1. The equilibrium of the cell was rather uncertain and was easily disturbed by a jar.

$\frac{dE}{dT}$ FOR THE CALOMEL CELL

The analysis of the temperature coefficient already applied to the amalgams of a concentration cell (Fig. 3) is equally successful when applied to the calomel cell. The following measurements of electrolytic thermoelectromotive forces were made by the writer many years ago by means of an extemporized potentiometer, which permitted direct measurements to one ten-thousandth volt only. The density of the zinc chloride solution was 1.395 g per cm^3 at 15°, and metallic zinc wire was used as the zinc electrode. One electrode was kept in an ice bath while the temperature of the other was raised by short steps.

A. $Zn \mid ZnCl_2 \mid Zn$

Temp.	Obs. emf	Comp. emf	Difference
8°.1	0.00490	0.00478	−12
10°.5	612	608	− 4
12°.3	750	726	−24
17°.7	1040	1044	+ 4
22°.2	1301	1310	+ 9
25°.8	1499	1522	+23
28°.6	1668	1687	+19
32°.1	1913	1894	−19
34°.5	2050	2036	−14
39°.1	2295	2307	+12

The mercury electrode was then subjected to the same treatment with the following results:

B. $Hg \mid HgCl \mid ZnCl_2 \mid HgCl \mid Hg$

Temp.	Obs. emf	Comp. emf	Difference
7°.1	0.00517	0.00486	−31
10°.6	730	726	− 4
12°.9	882	884	+ 2
16°.5	1125	1130	+ 5
19°.8	1358	1356	− 2
22°.8	1561	1562	+ 1
25°.3	1729	1733	+ 4
27°.9	1928	1911	−17
31°.8	2170	2178	+ 8
34°.1	2340	2336	− 4
36°.8	2554	2521	−33

For A, $E_1 = 0.000590\ t$; for B, $E_2 = 0.000685\ t$. Whence for this calomel cell

$$\frac{dE}{dT}=\frac{E_2-E_1}{t}=0.000095.$$

The table following shows the observed emf's compared with those computed from the equation

$$E = 1.0005 + 0.000095\ (t-15^\circ)$$

up to about 35°; for higher temperatures the observed values exceed the computed ones, perhaps because of the increased solubility of the calomel at those temperatures.

Temp.	Obs. emf	Comp. emf
10°.0	1.0001	1.00003
15°.0	1.0005	1.00050
17°.2	1.0007	1.00071
20°.4	1.0010	1.00101
23°.7	1.0013	1.00133
26°.7	1.0016	1.00161
30°.2	1.0020	1.00194
36°.4	1.0025	1.00253

The results are plotted in Fig. 5. The inclined line at the bottom marked E is drawn from the above equation and passes through 9°.75, where the emf of the cell is 1 volt. The observed emf's are plotted along this line.

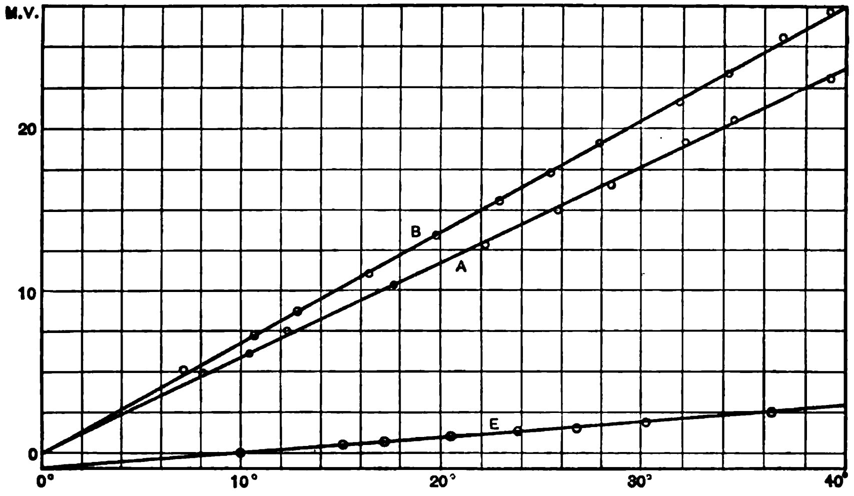

Fig. 5

A PAIR OF CALOMEL CELLS WITH CONSTANT EMF

The change of emf of the calomel cell with temperature is about 0.1 millivolt per degree and positive. The thermoelectromotive force at the mercury-mercurous chloride surface is thus higher than at the surface of the zinc.

Since the thermoelectromotive force between zinc sulphate and zinc amalgam increases as the concentration of the amalgam decreases, it is apparent that a calomel cell with a negative temperature coefficient is possible. Moreover, if the dilution of the amalgam produces a sufficient range in the thermoelectromotive force at its surface, it should be possible to make a calomel cell with a negative change of emf equal to 0.1 millivolt per degree. Such a cell in series with one set up with 10 per cent zinc amalgam would give a combined emf independent of temperature, at least over a range of 25 or 30 degrees.

A trial was made with a three-legged cell. One outer leg contained a 10 per cent zinc amalgam, the other an amalgam with about 0.8 per cent zinc; in the middle leg was placed mercury covered with mercurous chloride. The electrolyte was a solution of $ZnCl_2$, specific gravity 1.4. The cell was placed in a water bath and the potential difference between the two amalgams and the mercury as the positive electrode was measured at several temperatures. Let E_1 denote the emf of the cell with the 10 per cent amalgam and E_2 the other. A series of measurements is given in the following table:

Temp.	E_1	E_2	E_1+E_2	E_1-E_2
33°.3	0.99693	0.98456	1.98149	0.01237
30°.0	.99665	.98497	1.98162	.01168
26°.3	.99622	.98528	1.98150	.01094
22°.3	.99579	.98571	1.98150	.01008
18°.9	.99545	.98604	1.98149	.00941
14°.2	.99497	.98655	1.98152	.00842
9°.4	.99449	.98709	1.98158	.00740

These measurements were made within a period of two hours and the values correspond, therefore, to somewhat rapid changes of temperature. Nevertheless, E_1+E_2 remains nearly constant. The value of dE_1/dt is fairly represented by 0.000103 and dE_2/dt by -0.000103. If E_1-E_2 be denoted by E, then $dE/dt=0.000206$. The relation of these ratios to one another and to E_1+E_2 is shown graphically in Fig. 6.

SUMMARY

1. The general thermodynamic equation shows that when H is either zero or a constant, dA/dT is constant and $A=H+aT$.

2. A discussion of the expressions for A and H proposed by Nernst demonstrates that the term depending on the first power of T is not necessarily zero for A, as Nernst assumes it to be.

3. Concentration cells composed of zinc amalgams and either zinc sulphate or zinc chloride solutions, and cadmium amalgams

and cadmium sulphate solution, show a linear relation between their emf and temperature. This fact is contrary to Nernst's hypothesis.

4. dE/dT for these cells, and for others investigated by Richards, is a constant for each combination. H also is therefore constant and may be readily calculated from the Helmholtz equation for E.

5. The electrolytic thermoelectromotive force for zinc amalgams in contact with a solution of a salt of zinc is proportional to the temperature. In this instance, so long as there is no change of phase, H is zero and $E = aT$. When H is known for any two amalgams, the emf of the corresponding concentration cell may be calculated from H and the two thermoelectromotive forces.

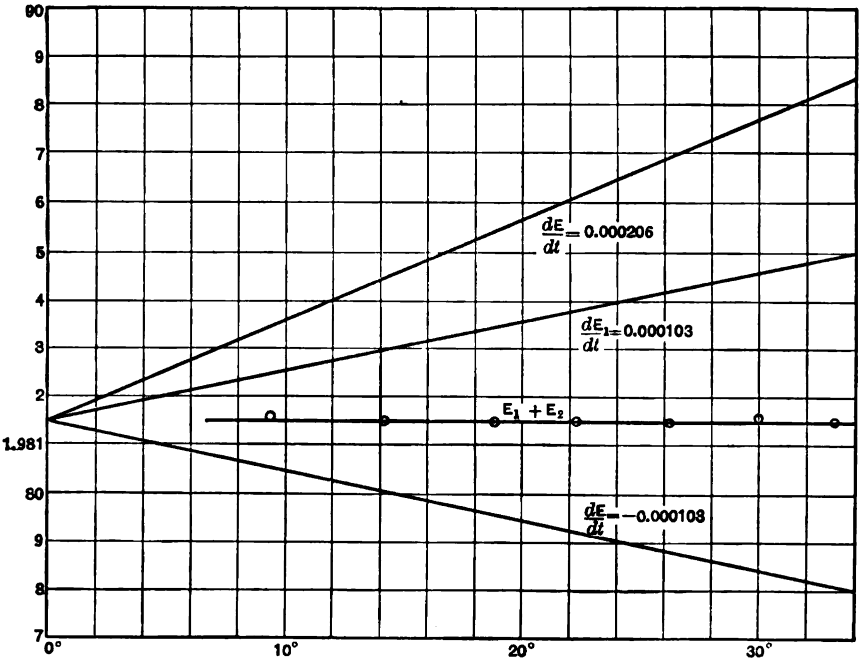

Fig. 6

6. By opposing the value of dE/dT for the amalgams by an equal and opposite value of dE/dT arising from a difference in the concentration of the electrolyte at the two electrodes, it is possible to

make a concentration cell independent of temperature. Its emf is derived entirely from the heat of dilution of the amalgams and of the electrolytes.

7. dE/dT for the calomel cell is positive, and is shown to be dependent on the difference between the thermoelectromotive forces at the two electrodes. By taking advantage of the fact that electrolytic thermoelectromotive forces vary with the concentration of amalgams, it is found possible to make a calomel cell with a negative temperature coefficient, numerically equal to that of the normal calomel cell, so that when the two are connected in series their combined emf is practically constant and independent of temperature over a range of 25 or 30 degrees.

The writer takes this opportunity to express to the Director of the Bureau of Standards his appreciation of the courtesies extended during the past few months, and his thanks for the privilege of carrying out the investigation described in this paper.

WASHINGTON, May 7, 1911.

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Fifth Annual Conference on the Weights and Measures of the United States.

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THE CAPACITY AND PHASE DIFFERENCE OF PARAFFINED PAPER CONDENSERS AS FUNCTIONS OF TEMPERATURE AND FREQUENCY

By Frederick W. Grover

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INTRODUCTION

The phenomenon of residual charges has long been observed and studied. The subject has been approached both by direct measurement of the quantity of electricity which appears, with the end in view of determining the laws governing its formation, and indirectly by measurement of the energy loss in dielectrics which exhibit this anomalous behavior.

To account for these evidences of a departure from the law of an ideal dielectric (according to which the charge at every moment is proportional to the instantaneous value of the impressed voltage) a number of theories of quite varied nature have been proposed, the most important of which will be considered below. Some of these are in qualitative agreement with the observed facts, but are at variance as regards the magnitude of the deviations from a perfect dielectric, while others give equations too complicated to admit of quantitative verification. Further, the great mass of the existing data refers to measurements with a steady emf, and under such a variety of conditions as regards temperature, length of charge, length of discharge, and previous treatment, as to render the task of deciding for or against any given theory well-nigh impossible.

With the employment of alternating current in the measurements a great simplification is gained, and at the same time a high degree of accuracy is attained. For, the condenser being regularly and rapidly carried through a definite cycle of charging and discharging, almost instantly reaches a condition of equilibrium, a condition not readily attained in measurements with a steady emf.

In view of these considerations, and following the development at the Bureau of Standards, of accurate and rapid methods for determining the loss of energy in a condenser, simultaneously with the measurement of the capacity, it was suggested to the author by Prof. Rosa, that an investigation of the change of capacity and absorption of condensers in which these changes are relatively large (for example, those employing paraffined paper as a dielectric) might throw some light on the points at issue.

As originally projected, the work was to include, first of all, an examination of a number of commercial condensers already at hand, to be followed by the construction and measurement of condensers prepared under definite specifications, to test the effect of variations in the method of construction on the behavior of the completed condenser.

Only the first part of this plan has been carried out. In October to December, 1906, a series of measurements at two frequencies, 33 and 100 cycles per second, was made on 12 different condensers, and at temperatures ranging from 10° to 35° in steps of 5°. This work was extended to other frequencies in July, 1907, the same condensers, together with one added to the previous list, being measured at 100, 300, 600, and 900 to 1000 cycles, the measurements at 100 cycles having been repeated to connect with the previous work. Owing to lack of time, only three temperatures, 15°, 25°, and 35° could be included in the last set. The work was interrupted at this point by the absence of the author from the Bureau, and following his return, other more pressing work has intervened to prevent the completion of the original plan. It has seemed, therefore, best to present without further delay, the results of the work already completed, together with such points of theoretical interest as have presented themselves in the discussion of the observations.

The first part of the present paper is accordingly devoted to a description of the method of measurement and the results of the observations, while the latter part deals with the theories of absorption, and a comparison of the observed facts with the theoretical requirements.

I. MEASUREMENTS

Only in a condenser having a perfect dielectric, i. e., one which is free from absorption and whose leads and plates have a negligibly small resistance, does the difference of phase between the current in the condenser and the sinusoidal emf impressed upon it equal the value of 90° required by theory. In all condensers which show the phenomenon of the formation of residual charge, the angle of advance of the current with respect to the impressed emf falls short of 90° by an angle ϕ whose sine is a measure of the energy dissipated in the condenser. This angle, which is usually small, is important for another reason. It is found to be, to a large degree, a measure of the relative magnitude of the residual charges of the condenser. In what follows, the angle ϕ will be designated simply as the *phase difference* of the condenser.

For the measurement of the phase difference, advantage is taken of the fact that, to obtain a balance in a Wheatstone bridge in which two of the arms contain two condensers whose capacities are being compared, two conditions must simultaneously be fulfilled, (*a*) the potential differences over the two condenser arms must be equal, and (*b*) these electromotive forces must have the same phase. The latter condition involves directly the difference in magnitude of the phase differences of the two condensers.

This matter has been considered in considerable detail in a previous paper,[1] where a number of alternating current bridge methods for obtaining at one and the same time the capacity and phase difference of a condenser, with reference to those of a standard were discussed, both from a theoretical and a practical standpoint. It will only be necessary here to recall such of the conclusions and formulas of the former paper as are applicable to the present measurements.

1. METHODS

In the earlier part of the work (frequencies 33 and 100) the Series Inductance Method (loc. cit., p. 390) was employed. In this method, the difference in the absorptions of the two condensers is balanced by a variable inductance in one or both of the ratio arms. In accordance with previous experience, the condenser whose constants were to be measured, was compared with the standard of reference—a condenser of known capacity and phase difference—by substitution, the unknown and the standard being successively balanced against an auxiliary condenser C_2 (Fig. 1) whose

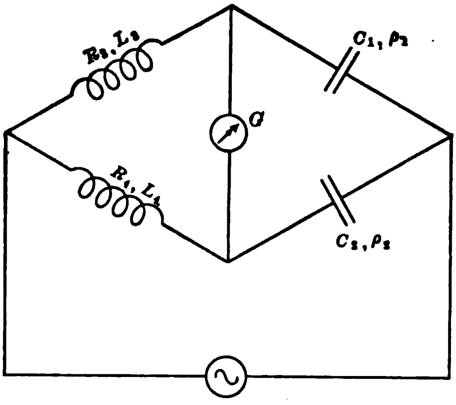

Fig. 1

NOMENCLATURE

R_3 and R_4 are resistances associated with the inductances L_3 and L_4 of which L_3 is variable. ρ_1 and ρ_2 are fictitious resistances in series with the condensers C_1 and C_2 which would produce the same shift of phase as the absorptions of the condensers.

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[1] This Bulletin, 3, p. 371; 1907.

value does not need to be known, but whose capacity should be of the same order of magnitude as those of the other two condensers. This procedure has the advantage of eliminating capacity effects between the various parts of the bridge and the earth and between one another, which effects can become a fruitful source of error at the higher frequencies.

The conditions for balance of the bridge shown in Fig. 1, when the substitution method is used, are

$$\frac{C_1'}{C_1''}=\frac{R_3''}{R_3'}\left[1+\tan(\varphi_1'-\varphi_1'')\left\{\tan\varphi_2-\frac{pL_4}{R_4}\right\}\right] \quad (1)$$

$$\tan(\varphi_1'-\varphi_2'')=\frac{pL_3'}{R_3'}-\frac{pL_3''}{R_3''} \quad (2)$$

The correction term in the formula for the ratio of the capacities can be made very small, even in the case of condensers with large absorption, by so choosing L_4 and R_4 that the angle of lag in that arm of the bridge approximately equals the phase difference of the auxiliary condenser. This is, however, not important, since in the case of condensers whose absorption is sufficiently large to give to tan $(\varphi_1'-\varphi_1'')$ an appreciable value, the capacity is always observed to be so susceptible to minute temperature changes and slight variations in the frequency as to obscure the small effect of this correction term.

For example, with a paper condenser of moderately large absorption, and with the constants of the bridge used as follows:

$p=600$, $L_2=10$ millihenrys, $R_4=1200$, $\varphi_1'-\varphi_1''=30'$, $\varphi_2=4'$

the correction to the capacity is only

$$\tan 30'\left\{\tan 4'-\frac{6}{1200}\right\}=-0.000029$$

which is practically negligible with such a condenser.

The later work was carried out almost exclusively by means of the Series Resistance Method (loc. cit., pp. 380, 387), in which the difference in absorption is compensated by inserting resistance in series with one or both of the condensers. This arrangement was used as a substitution method as in the case of the Series Inductance Method.

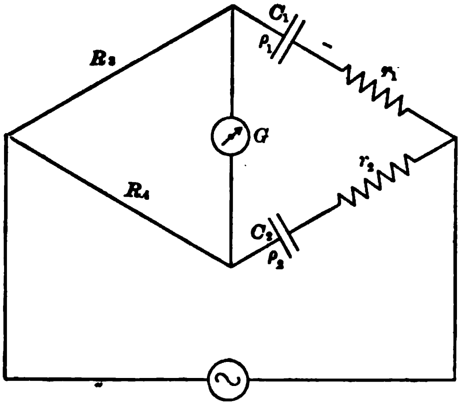

Fig. 2

NOMENCLATURE

R_3 and R_4 are the resistances of the ratio arms. C_1 and C_2 are condensers whose fictitious resistances are ρ_1 and ρ_2, and r_1, r_2 are resistances used in balancing the differences in the phase differences of the condensers. The standard and the unknown are successively inserted at C_1 and the values of R_3 and r_1 for balance are respectively R_3'', r_1'' and R_3', r_1'.

The conditions for balance are then very approximately

$$\frac{C_1'}{C_1''}=\frac{R_3''}{R_3'} \tag{3}$$

$$\tan(\varphi_1'-\varphi_1'')=pC_1''(r_1''-\frac{R_3''}{R_3'}r_1') \tag{4}$$

This method has the advantages over the preceding for work with condensers of relatively large phase difference, that it is much easier to vary the series resistance over a large range (as is necessary when testing condensers whose phase differences cover a large range of values) than it is to vary the inductance L_2. For instance, with the condensers here examined it was found to be necessary to obtain values of the inductance variable in rather small steps between a few millihenrys up to about 1 henry in the case of the worst condenser. With the fixed values of inductance usually at hand it becomes a tedious process to find the combination of fixed values which, taken together the variable inductance used, will give a balance of the bridge within the range of the variable.

Some difficulty was experienced in the work at the higher frequencies in obtaining trustworthy values of the phase differences. This was found to be due to the fact that the ratio coils were mounted in metal cases. Arranged thus, the capacity of these coils with respect to their surroundings is so large, that at these high frequencies, even the small differences in the potential of the galvanometer terminals necessitated by the small difference of resistance in the ratio arm when passing from the standard to the unknown are sufficient to materially change the phase of the current in the arms of the bridge, and thus vitiate the value determined for the phase difference. Evidently this effect, which is negligible at the lower frequencies, is aggravated by any cause which gives the resistance coils a larger capacity, and its magnitude, other things being equal, will vary as the absolute values of the ratio arms are changed. Further, the fact that these paper condensers had capacities varying more from the values of the standards of comparison than is usual in precision work, tends to aggravate this effect.

It was found, however, that by using unmounted ratio coils of values not greater than about 500 to 1000 ohms, only the relatively small variable part of the ratio arm being included in a metal case, the values of the phase difference determined became sensibly independent of the magnitude of the ratio arm.

The resistances r, used in the condenser arms, were usually small, and were taken from dial boxes, a slide wire in series with the latter enabling the changes in the resistances of these arms to be measured to 0.001 ohm.

The effect of small resistances in the leads becomes very important in the measurement of the phase differences of condensers of 1 microfarad and greater at the higher frequencies used. For example, a resistance of only 0.02 ohm in the leads of a 1-microfarad condenser at 1000 cycles per second, increases the measured phase difference by 26″. The correction is proportional to the capacity and the frequency. This resistance was kept as small as possible by the use of stout wires soldered where practicable, and the actual resistance external to the condenser terminals was determined and corrected for in every case. At the lower frequencies some of the measurements were made using a two-way key to facilitate changing from the unknown to the standard. This was, however, abandoned in all work above 100 cycles, because of the chance of uncertain contacts in the condenser arm, which might prove to be the source of an appreciable error in the determination of the phase difference.

Measurements were always made in pairs, using two different values of the ratio arms, both with the standard and the unknown. This procedure is well worth the additional time required, even when a large number of condensers are to be compared, because of the check thereby afforded, both on the measurements and the calculations. The latter are by no means complicated, and consume no undue amount of time. When, however, as in the present instance, many measurements are to be made, it would be a saving of time and would facilitate the detection of errors during the course of the observations, to use the arrangement devised by Curtis[2] (since the completion of this work) which allows the capacity of the unknown condenser to be read directly from the setting of the bridge.

2. APPARATUS

The current for the comparisons at 33 and 100 cycles was taken from a ½-kw motor-generator set, driven from a storage battery, the variations of the speed desired being obtained by a variable rheostat in the armature circuit of the motor. The higher frequency currents (300, 600, 900–1000 cycles) were supplied by three generators of a series designed to give frequencies corresponding to the fundamental and the odd harmonics (including the fifteenth) of 60 cycles. This set of alternators was specially designed for the Bureau of Standards for researches requiring a wide possibility of variation of wave forms of known composition.

Vibration galvanometers were employed to indicate when the bridge was balanced. Since an instrument of this type is highly sensitive only for a frequency corresponding to the natural period of torsional vibration of the suspended system, and responds only in a very small degree to currents of other frequencies, the emf does not have to be closely a sine wave. The galvanometer if tuned to the frequency of the fundamental, indicates when the bridge is balanced for the latter, although this condition does not hold for the other components.

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[2] This Bulletin, 6, p. 439; 1910.

The importance of this property (which is not shared by the telephone) in measurements like the present, can not well be overestimated. In the case of a condenser circuit, all existing distortion of the emf wave is magnified in the current wave by the capacity. Since, now, unless the phase difference of both condensers is zero the conditions for balance of the bridge are different for each harmonic, any instrument like the telephone must always show the presence of current of some frequency, however the arms of the bridge are varied and with condensers of large absorption the minimum current will be very appreciable. The position corresponding to the minimum of the current will not, in general coincide with the balance point of the fundamental, and the sensibility of the setting is reduced by the presence of the residual of current.[3] These effects (small with condensers of small and nearly equal phase differences) are so great with condensers of large absorption, as to render the use of the telephone as indicating instrument unsatisfactory, if not impossible. In the present instance, at the lowest frequency, the difference in the balance point for the fundamental and that of the harmonics was in a few cases so great, as actually to produce appreciable forced vibrations of the galvanometer corresponding to the residual currents of harmonic frequencies. In such a case inductance may be used in the main circuit to annul the effects of the harmonics, or capacity may be introduced to produce more or less complete resonance of the circuit for the fundamental. With such poor condensers, however, this is hardly worth while, since it will be found that the balance is so sensitive to minute changes of the frequency, and the slight heating of the condenser by the *measuring current* causes such a notable drift of the setting for balance, as to enable snap readings only to be obtained.

For the measurements at 33 and 100 cycles two galvanometers of the Rubens type[4] were used; for the higher frequencies, instruments of the Wien type.[5] The latter form of vibration galvanometer is considerably the more sensitive, but suffers from the disadvantage that its resonance peak is inconveniently sharp, and its damping relatively poor. The Rubens galvanometer is free from these difficulties, and is very satisfactory for all work which does not demand unusual sensibility, but so far as is known to the author it is not made for frequencies higher than about 200 cycles per second. Recent experience indicates that the Campbell form [6] of vibration galvanometer combines with a greater sensibility a larger range of attainable frequencies than the Rubens.

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[3] This Bulletin, **3**, p. 376; 1907.

[4] Wied. Ann., **56**, p. 27; 1895.

[5] Ann. der Phys., **4**, p. 425; 1901.

No attempt was made to adjust the resonance frequencies of the Wien galvanometer closely to the exact values desired. It is a tedious operation to adjust the system of a galvanometer of this type to resonance with any prescribed frequency, but it is fairly easy to approximate the desired frequency in a very few trials, and to vary the speed of the machine until the current is in resonance with the period of the galvanometer. It is a simple matter to correct the observed results for the small difference between the actual and the desired frequency.

3. CONTROL AND MEASUREMENT OF THE FREQUENCY

Although a precise knowledge of the value of the frequency is not requisite in these measurements, means must be provided by which the resonance frequency may be located and thereafter reproduced at will. This is especially important when a setting is to be made on a condenser with an appreciable phase difference. If the speed of the machine fluctuates, the balance of the bridge will drift in a manner very annoying if many settings are to be made. Further, with the Wien galvanometer, the resonance peak is so sharp that a variation of the frequency by only one-tenth of a per cent from the resonance value reduces the deflection (other things being equal) to less than one-half of its value, so that it is often easy to obtain a spurious balance due to the reduced sensibility of the galvanometer. In any case it becomes very arduous to balance the bridge with a continually varying sensibility.

With the lower frequencies the speed of the alternator was adjusted by an auxiliary Maxwell bridge, the condenser being charged and discharged by a rotating commutator direct connected to the shaft of the alternator.[7] This method not only allows the resonance point to be very exactly identified and reproduced, but with a calibrated condenser the corresponding absolute value of the frequency may be determined with great precision.[8]

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[6] Phil. Mag. [6], 14, p. 794; 1907.

At the beginning of the day's work the vibration galvanometer is connected to a simple Wheatstone's bridge (or any other bridge whose balance does not depend on the frequency of the current). Having nearly balanced the bridge, so that the galvanometer shows only a small deflection, the speed of the generator is varied until the resonance frequency is attained, as evidenced by a sharply defined maximum deflection of the galvanometer.

This speed being maintained constant by one observer, a second observer balances the Maxwell bridge by adjusting the resistance in one of the arms. This having been accomplished, the resonance frequency can thereafter be reproduced and maintained constant by one observer at the Maxwell bridge whenever the alternating current bridge is to be balanced by the second observer.

This method was not found practicable in the case of the measurements at the higher frequencies, where the alternators were in a separate building from the bridge. Well-insulated leads were carried between the two buildings, but, owing perhaps to variations in the capacity between the leads and the earth, the galvanometer deflection varied in an erratic manner, and the attempt was abandoned.

The following method, suggested by Prof. Rosa was found very effective, and has the advantage that it is independent of any adjustment of brushes, an advantage not to be overlooked when the alternator is in another room from the observer.

This method depends on the use of a double electrodynamometer having two movable coils fixed to the same axis, each being placed in the field of a pair of fixed coils. In the instrument used in these measurements a taut suspension of phosphor bronze strip stretched between spiral springs at both top and bottom and provided with a damping vane insured a dead-beat movement, one of the requisites for the success of the method. The actual instrument was inexpensive and of only moderate sensibility, but gave a very satisfactory performance.

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[7] This Bulletin **1**, p. 153; 1904. [8] This Bulletin, **1**, p. 181; 1904.

The whole or a portion of the supply voltage is impressed on two circuits in parallel (Fig. 3), in one of which is connected in series a condenser, the two movable coils m_1 and m_2 and one pair f_2 of the fixed coils of the double electrodynamometer, and in the other a large inductance L and the remaining fixed coils f_1. Fig. 4 shows the relative phases of the currents in the dynamometer. The torque between the fixed coils f_1 and the movable coils m_1 is proportional to $i_1 i_2 \cos \phi$ and that between the fixed coils f_2 and the movable coils m_2 is proportional to i_1^2, where i_1 and i_2 are, respectively, the currents in f_1 and f_2. But $i_1 \propto pC$ and $i_2 \propto \frac{1}{pL}$ provided the reactances of the coils of the dynamometer are small in comparison with those of the condenser and the inductance coil. The torque t_1 is therefore dependent to only a slight degree on the frequency, while the torque t_2 varies nearly as the square of the frequency. The connections being so made that the two torques t_1 and t_2 are opposed to one another, it is possible by adjusting the capacity or inductance, or both, to bring the deflection of the dynamometer to zero. This balance having been made for a given frequency, it is evident that any change of the frequency will disturb the balance and, what is more, the deflection occurring with decreasing frequency will be in the opposite direction to that with increasing frequency.

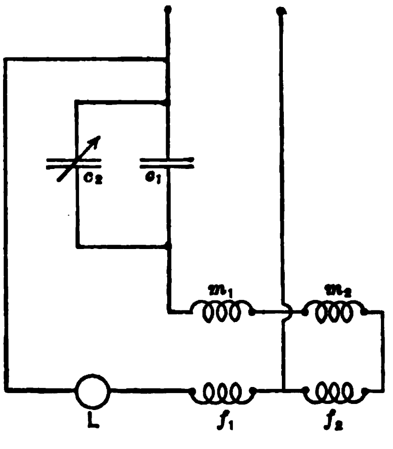

Fig. 3

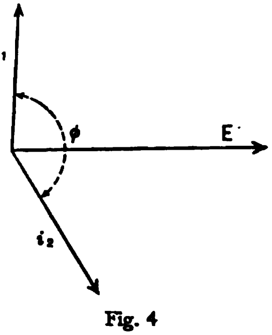

Fig. 4

The adjustment of the circuits is, in practice, best made as follows: Having adjusted the frequency roughly, a suitable inductance is found, such that, with the voltage used, when the circuit is closed through the inductance, the fixed coils f_1 and the movable coils in series, a deflection of about 1 meter is produced. This current is next broken and a current passed through the fixed coils f_2, the movable coils, and a condenser variable in steps, all in series. The capacity of this latter circuit is adjusted until the deflection obtained has about the same magnitude as that previously obtained with the inductance in circuit. The fixed coils f_1 in series with the inductance coil are then shunted between the terminals of the circuit containing the condenser, care being taken that the two torques due to the action of the two currents are in opposition. It is now easy by continuous variation of the capacity or the inductance, or both, to bring the dynamometer deflection to zero. By increasing the impressed voltage, the sensibility may be increased within limits compatible with the safe current carrying capacity of the movable coils of the dynamometer. The correct frequency for resonance with the galvanometer having been reached and held constant by the use of a variable resistance in the field circuit of the alternator, a second observer balanced the dynamometer circuits. He was thereafter in a position to keep the frequency at the correct value (by manipulating the resistance in the motor field circuit), while the other observer made the settings on the alternating current bridge.

With this method of speed control, the resistance of the coil L does not have to be kept negligibly small, as was assumed for the sake of the demonstration, but the angle of lag of this circuit should be kept large enough to make the phase difference between i_1 and i_2 (Fig. 4) considerably greater than 90°, in order that the torque t may not be unduly decreased by the approach to a condition of quadrature of the two currents.

The actual value of the resonance frequency was, in the present instance, sufficiently well determined by measuring the speed of the alternator by means of a speed counter. Greater precision may, however, be attained, when desired, by the use of an auxiliary bridge containing resistances in three of its arms, and a known capacity in series with a calibrated variable inductance in the fourth arm. The frequency being held at the value which is to be measured, by means of the dynamometer arrangement, a second observer balances the auxiliary bridge (which is supplied by the same source) by alternately varying the inductance and resistance of its fourth arm. For this measurement the same vibration galvanometer is used as in the main measurements, its frequency of vibration being of course the frequency which it is desired to determine. The frequency is calculated from the capacity and inductance necessary to balance the auxiliary bridge, using the familiar relation $p^2LC=1$. This extremely sensitive method for determining the value of a frequency is evidently applicable to any case where it can be maintained constant by auxiliary apparatus. The most perfect arrangement is to use for detecting the balance of the auxiliary bridge a vibration galvanometer whose period of resonance is adjusted to the period of the current whose frequency is to be measured, but with a fairly pure wave form, a telephone could probably be used where a moderate sensibility is sufficient.

4. CONTROL OF THE TEMPERATURE

The condensers were kept in a galvanized iron tank 58 x 50 x 50 cm surrounded by a water jacket on all sides, except the top, which was insulated by a layer of hair felt 3 cm thick. The quantity of water in the jacket (about 100 liters) was so large that its temperature when within 5° of the temperature of the room, changed very little from day to day, requiring thus little or no regulation. The extreme temperatures, 10° and 35°, were obtained by filling the water jacket with water whose temperature was about 3° lower or higher, respectively, than the desired temperature, about 24 hours before it was desired to make the measurements. From previous experience this was believed to be long enough to insure the condensers taking up the temperature of the bath which after this interval was at closely the temperature desired. Since in every instance check measurements, made after an interval of several days, agreed well with those made 24 hours after adjusting the temperature of the bath, this assumption was undoubtedly sufficiently well justified. Owing, however, to the creeping of the temperature of the jacket at 10° and 35° during the four or five hours, required for a complete set of measurements, the temperature of the condensers was uncertain by a few tenths of a degree, at these extreme temperatures, which may perhaps be a sufficient explanation for the fact that the curves do not repeat themselves perfectly at 35°, where uncertainties in the temperature are of the greatest effect. The results are, however, not seriously affected by this source of error. Measurements were made at two frequencies each evening, but owing to the number of condensers studied, two evenings were required to finish the list in the earlier work where the Series Inductance Method was employed. The use of the Series Resistance Method in the later series reduced materially the time required for the measurements. In the work at 33 and 100 cycles, the temperatures followed the order 19°, 25°, 30°, 34°, 20°, 15°, and 10°. The values observed at 20°, both with ascending and descending temperatures, agreed so well, that in the later series at the higher frequencies, measurements were made at 15°, 25°, and 35° only, without repetition. Settings were made at 100 cycles in every set, so as to give a check on the constancy of the condensers during the progress of the work, as well as to more accurately obtain the effect of frequency, unaffected by any correction for temperature. Most of the condensers showed a constancy over the interval of seven months between the first and second parts of the work, which was better than had been expected.

5. CONDENSERS STUDIED

The following table summarizes all of the data available on the details of construction of the condensers tested. In all except the condensers designated as $Be_{1,5}$ and $Be_{3,4}$ the dielectric is paraffined paper; in the two exceptions the paper had been impregnated with beeswax.

Of these condensers S_3, S_6, and S_{10}, t_3, t_{17}, and W_a each is completely sealed in the inclosing metal case, the terminals of the first group being brought out through insulating bushings. t_3, t_{17}, T_2, and W_a were especially designed for telephone work; the others for general laboratory use.

None of these condensers are clamped. In *Cp*, however, the space between the condenser and the cover of the box is occupied by strips of cardboard. The condenser *Mp* quite accurately fills its containing box, and in *Lp* two blocks of wood have been introduced, which fit rather tightly between the condenser and the cover of the box. *SH* does not fit its case at all tightly. In view of these facts it may be remarked in passing that the majority of the condensers suffered permanent changes of capacity or phase difference, or both, during the observations. These changes were for the most part unimportant. Of the condensers, T_2 and W_a showed changes in the capacity only, W_a to about 0.1 per cent and T_2 a permanent decrease of about 1 per cent. $Be_{1,5}$ exhibited a decrease in the phase difference of perhaps 10 per cent at the lower frequencies, but no noticeable change in capacity. Of the remaining condensers, the following permanent changes were noticed: *SH*, increase in capacity 6 in 10 000, increase in phase difference of about 5 per cent; *Cp*, increase in capacity 12 in 10 000, increase in phase difference about 10 per cent; S_8, a

TABLE I

Designation	Where made	Box	Construction	Paraffin		
				Color	Softened	Melted
S_3, S_8, S_{10}	U. S.	Metal	Flat sheets, 25 cm x 30 cm	White	(?)	(?)
Cp	France	Wooden	Flat sheets, 25 cm x 30 cm	Gray	36°	52°.5
Lp	U. S.	Wooden	Flat sheets, 15 cm x 20 cm	Yellow	30°(?)	51°
Mp	England	Wooden	Roll, 20 cm wide, four sections	Yellowish white	48°	57°
SH	Germany	Wooden	Sheets, 15 cm square	Very white	48°	58°
T_2	U. S.	Metal	Paper and tin foil wound together on wood	Dark gray	32°	46°
W_a	U. S.	Metal	Strip, 10 cm wide, rolled up			
$Be_{1,5}$, $Be_{3,4}$	U. S.	None	Sheets, 10 cm x 15 cm			
t_3, t_{17}	U. S.	Metal	Strip, 8 cm wide, rolled up			

decrease in phase difference of about 6 per cent, a decrease in capacity of 0.1 per cent, noticeable at 100 cycles only.

There are two cases which may occur, viz, a mechanical change in the condenser, such as a change in the configuration of its parts, due to a springing of its plates, while the dielectric is somewhat plastic at the higher temperatures, and second, some change in the nature of the dielectric. Of these two effects, the first should not involve the phase difference, but, on the other hand, any change in the phase difference tends to produce a change in the measured capacity, an increase in phase difference giving rise in general to an increase in the capacity. In a number of the above instances, these effects are qualitatively substantiated, although occasionally the effect of a change of phase difference seems to have produced no measureable influence on the capacity. The hypothesis of a change in capacity due to the relieving of stresses while the dielectric is somewhat plastic gains probability in the light of the comparatively low softening point observed for some of the samples of paraffin taken from these condensers (see Table I), although the observed changes do not follow very closely these observed temperatures of noticeable plasticity.

6. METHOD OF PRESENTING THE RESULTS

The following table of the results of a single day's observations at a single frequency, will illustrate the magnitudes of the observed quantities, and serve to indicate the concordance obtained with different values of the ratio arms.

In these observations the various sections of the mica condenser *B*, whose capacity and phase difference at various temperatures and frequencies had previously been very accurately determined, were made the basis of the work. The condensers 7763 and 7766 were also used in conjunction with the former, and since these last condensers had not been previously studied at the higher frequencies, their values were connected with those of condenser *B* by direct comparison on the day of observation (as in the above table).

In Table II the capacities in column 4 were calculated from the observed values of R_3 and the known value of the standard, which is placed last in each group of comparisons. From the observed values of r_1 in the sixth column the differences in phase referred to the phase difference of the standard were calculated by formula (4) and are tabulated in the seventh column. The last column contains the absolute values of the phase differences of the condensers, computed from the known phase differences of the standards.

TABLE II

July 12, 1907. Frequency 314 cycles. Temperature 25°8

Condensers		R_3	Capacity (observed) mf	r_1 ohms	$\phi_1'-\phi_1''$	Phase diff.
Auxil.	Test					
					° ′ ″	° ′ ″
L	S_{10}	598.50	3.03727	2.474	11 31	
+7764	S_{10}	1098.90	30	2.508	48	13 0
+7765						
L	S_6	575.06	3.14525	0.765	46 3	47 24
+7764	S_6	1061.16	29	0.806	6	
	7766	600.33	(3.01286)	3.049		(1 20)
+7765	+B+	1107.80		3.094		
	7763					
7764	S_3	599.86	1.60952	1.933	12 55	
$+L_{06}$	S_3	1106.97	51	2.007	13 6	14 10
	7766	600.49	(1.60784)	3.118		(1 10)
	$+B_{0.6}$	1108.12		3.208		
7764	t_{17}	567.34	1.91462	2.356	3 36 9	
$+L_{0.7}$	t_{17}	1047.08	38	2.493	38 43	3 38 0
	T_2	610.40	1.77959	15.007	65 39	
	T_2	1126.46	48	15.066	51	66 53
	7766	600.56	(1.80871)	20.109		(1 8)
	$+B_{0.8}$	1108.25		20.184		
L	SH	591.70	1.02207	5.226	34 42	
L	SH	1091.91	06	5.362	48	35 45
L	Mp	615.46	0.98262	9.721	6 6	7 6
L	Mp	1135.78	58	9.771	53	7 53
L	Lp	628.08	0.96289	6.552	28 8	
L	Lp	1159.11	80	6.710	9	29 8
L	7766	602.41	(1.00391)	10.410		(1 0)
L	7766	1111.65		10.563		

TABLE II—Continued

July 12, 1907. Frequency 314 cyles. Temperature 25°8—Continued

Condensers		R_3	Capacity (observed) mf	r_1 ohms	$\phi'_1-\phi_1''$	Phase diff.
Auxil.	Test					
					° ′ ″	° ′ ″
L	W_a	587.47	1.02940	6.221	27 11	
L	W_a	1084.14	31	6.361	7	28 26
L	7763	602.24	1.00411	10.302	0 24	
L	7763	1111.36	10	10.436	24	1 44
L	7766	602.36	1.00390	10.410	−0 19	
L	7766	1111.56	92	10.558	− 15	1 0
L	B	601.80	(1.00485)	10.354		(1 17)
L	B	1110.52		10.488		
$L_{0.6}$	t_3	542.35	0.66868	6.9	9 12 0	9 37 0
$L_{0.6}$	t_3	1005.35	569	10.4	28 0	
$L_{0.6}$	$B_{0.6}$	600.50	(0.60393)	150.763		
$L_{0.6}$	$B_{0.6}$	1108.16		150.994		(1 17)
$L_{0.5}$	$Be_{1,5}$	530.40	0.56893	3.237	58 48	
$L_{0.5}$	$Be_{1,5}$	1067.07	98	3.513	40	59 44
$L_{0.5}$	$Be_{3,4}$	566.91	0.53230	7.355	44 43	
$L_{0.5}$	$Be_{3,4}$	1046.13	31	7.623	45	45 44
$L_{0.5}$	Cp	623.28	0.48415	12.615	29 50	
$L_{0.5}$	Cp	1150.24	12	12.916	50	30 50
$L_{0.5}$	7766_r	601.32	(0.50184)	20.921		(1 0)
$L_{0.5}$	7766_r	1109.64		21.211		
$L_{0.5}$	7766_r	1209.83		21.194		

It has seemed most practicable and conducive to clearness not to tabulate the whole mass of the observed data, but rather to embody the results in curves, which shall give, along with the numerical values, a clear picture of the variations of the observed quantities with varying temperature and frequency. Accordingly, the sum of the results on each condenser is incorporated in two sets of curves, which present (a) the capacity and phase difference as functions of the temperature, with the frequency as variable parameter, and (b) the capacity and phase difference as functions of the frequency, with the temperature as variable parameter. To distinguish between the curves of capacity and phase difference, the latter are drawn as dotted lines, while the curves of capacity are in full lines. These 26 sheets of curves have been numbered for ready reference.

Unfortunately the differences in the values of the constants of the various condensers are of such widely different magnitudes as to make it impracticable to draw all the curves to a uniform scale, without in certain instances obscuring points of interest. The scale of each curve is, however, clearly indicated, and to lend clearness and emphasize the relations between the different scales, the curves for the mica condenser *B* are drawn to scale on each sheet.

7. CURVES OF RESULTS

A casual inspection of the curves of figures 5 to 30 suffices to show how greatly the different condensers vary among themselves in their constants. The relations connecting the capacity and phase difference with the temperature and frequency are far from simple, and their detailed consideration in the light of the various theories of absorption will be taken up in the second part of the paper. The following points are, however, of importance from a practical standpoint.

(1) The **changes of capacity** with the frequency and temperature are much larger than are observed with mica condensers, and are very appreciable in every case. The amount of change is in general larger with those condensers which have a large phase difference. In the case of the poorer condensers studied (Figs. 21–30) the changes of capacity, referred to the value at the highest frequency and lowest temperature, where the effects of absorption are smallest, range from 5 to 60 per cent, for the temperatures and frequencies studied.

(2) The **phase differences** observed range from about 6′ in the case of *Mp* (Figs. 5 and 6) to the enormous value of about 22° with the condenser t_8 (Figs. 29 and 30). The phase difference of a good mica condenser may be as low as 15″ at the higher frequencies, and usually lies under 3′ even at the higher temperatures and lower frequencies.

(3) The **temperature coefficient** of the capacity is in some cases negative and nearly constant (Figs. 5, 7, and 9) and in others

positive and rapidly increasing with the temperature (Figs, 15, 17, 21, 25, 27, and 29). In still other condensers the temperature coefficient is negative at the lower temperatures and higher frequencies, and tends to become positive with increasing temperature, especially at the lower frequencies (Figs. 17, 19, and 25). The negative temperature coefficient occurs as a rule with those condensers having small phase differences, and the coefficient, although larger than that of a good mica condenser, does not exceed about 5 parts in 10 000. On the other hand, the positive temperature coefficients, which are usually found in condensers having large phase differences, are in many cases of the order of 1 per cent at the higher temperatures and lower frequencies.

(4) **Change of capacity with frequency.**—With increasing frequency the capacity falls off, at first rapidly and then more slowly, and tends to reach a limiting value, asymptotically, which represents the value of the capacity as unaffected by absorption. With a given condenser these changes with the frequency are larger at the higher temperatures, and in the case of condensers with large phase difference may become very large (Figs. 22, 24, 26, 28, and 30).

(5) **Change of phase difference with frequency.**—In the majority of cases the phase difference increases with rising temperature, but whereas the change is small and nearly linear in the case of mica condensers, paper condensers show as a rule a rapid rise of the curve at the higher temperatures and lower frequencies, and with some of the poorer condensers here studied these effects are enormous. The change of the phase difference with the frequency will be considered more in detail below.

The above considerations will make clear the fact that paper condensers are, at best, poorly adapted to serve as standards of capacity, and even in work of small precision should be excluded, unless a preliminary study has shown that the capacity is sufficiently constant over the range of temperatures and frequencies in which it is to be used.

From the paper of Curtis[9] it appears that the capacity of mica condensers when tested with direct current is far more dependent on the conditions of the experiment than with alternating current. It would therefore appear from the foregoing curves with alternating current, that the use of paper condensers as standards in measurements with direct current, and in fact in all direct-current work where a knowledge of the capacity is desired, is to be condemned. This conclusion has been abundantly borne out in work with the ballistic galvanometer at the Bureau of Standards and elsewhere. It is no uncommon experience to find condensers whose apparent capacity with periods of charge and discharge of several seconds is double that observed with a quick charge and discharge, while the value under the same conditions of charge and discharge increased with every successive charge. These effects are of course smaller in any given case with short periods of charge and discharge, but the results of Prof. Zeleny (Phy. Rev., 1911) with charging and discharging periods of only a few thousandths of a second, show that even then the capacity and temperature coefficient are appreciably affected by the conditions of the experiment.

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[9] This Bulletin, 6, p. 457; 1910.

8. EFFECT OF RESISTANCE EXTERNAL TO THE CONDENSER

The curves connecting the values of the capacity at different temperatures and frequencies are so smooth as to indicate that the errors of observation are of small effect. The curves showing the change of phase difference with the frequency are, on the contrary, rather irregular; instead of falling off asymptotically with increase of frequency, as is the case with mica condensers, the phase difference in some cases actually increases with the freqeuncy over a moderate range, and begins to fall off again, if at all, only at the highest frequencies. Although in some of these cases, as we shall see later, there is evidence to show that the phase difference should be larger at frequencies of the order of 300 cycles than at 100 cycles, this form of the curve is probably mainly due in the majority of cases to the effect of the internal resistance of the condenser.

As already stated, the resistances of the leads from the condenser to the bridge were carefully measured, and a correction applied to the measured value of the phase difference. If, however, there be in addition an appreciable internal resistance in the condenser, the measured values of the phase difference will still be too large, by a value which is proportional to the frequency, to the value of this resistance, and to the capacity of the condenser. This correction to the phase difference is given by the formula tan $\theta = pC\rho$ as before. Trial has shown that in the case of most of the curves an approximate value of the resistance ρ may be found, which will give a corrected curve of the phase difference with the frequency, falling rapidly at the lower frequencies, but decreasing asymptotically at the higher frequencies. The following table shows the values thus found, together with the specification of the curves from which they were derived:

TABLE III

Condenser	Temperature	ρ ohms
SH	15° and 25°	0.15
Mp	15°, 25°, and 35°	0.07
t_{17}	15° and 25°	1.0
$Be_{3,4}$	15°, 25°	1.0
T_2	15°, 25°	0.25
Lp	15°	0.50
Lp	25°, 35°	0.20
Cp	15°, 25°	1.3
S_6	15°, 25°	0.25
W_a	15°, 25°, 35°	1.92
S_8	15°, 25°	0.21
S_{10}	35°	0.08
S_{10}	25°	0.20
t_8	15°, 25°	3.6
$Be_{1,5}$	15°, 25°	0.7

These values of ρ are in most cases quite definite. It seems nevertheless impossible to derive values of ρ for Mp, S_{10}, and S_8, Figs. 5–10, which shall hold for all the curves and for each curve over the whole range of frequency. It is just these condensers, however, for which there is theoretical evidence that the shape of the curves of phase difference φ with the frequency is more complicated than the simple form here assumed.

This extra resistance ρ has been calculated on the assumption that it is entirely due to causes external to the plates of the condenser, viz, lead resistances between the binding posts and the plates, and contact resistances where the tin foil is welded together and joined to the leads. Since, with the most of these condensers, the plates are all in parallel, the plate resistance should be practically negligible. The three telephone condensers t_8, W_a, and t_{17}, Figs. 29, 30, 11, 12, 27, and 28 are made by rolling up together two or more sheets of tin foil with the dielectric between them. Since the number of sheets in parallel is small, and each sheet is very long and thin the plate resistance should form an appreciable part of the whole resistance, and this seems to be borne out by the large value of ρ found in these cases. This explanation is confirmed by some recent measurements of Curtis on telephone condensers, all from the same maker, in some of which connection was made at frequent intervals along the edge of the plates. The phase difference in this latter case decreased with increasing freqeuncy, while with those in which the leads were attached to the ends of the plates only, the phase difference was considerably larger at the higher frequencies than at the lower.

The importance of the internal resistance of a condenser in shifting the phase does not seem to have received general attention. In many cases the energy loss in this resistance becomes of greater importance than that in the dielectric. (In the case of the condenser W_a, Fig. 12, the I^2r loss in the plates and connections is, at a frequency of 900, about three times as great as the loss in the dielectric). Not only does this cause unnecessary heating of the condenser, with consequent change of its capacity, but the apparent phase difference increases rapidly with the frequency.

II. THEORIES OF ABSORPTION

The question of the explanation of the phenomenon of absorption has long occupied the attention of the physicists, and much has been published on the subject. In the small space here available it is, however, necessarily impossible to give a complete view of the theories which have been advanced, and the evidence which has been collected for or against these various hypotheses. The author has been obliged to confine his attention to what seem to be the most hopeful theories in the light of the present experiments, and would direct the reader who wishes to gain a more complete knowledge of the subject to the really admirable bibliography of the subject by von Schweidler (appended to his article on

Die Anomalien im Verhalten der Dielectrika, Ann. der Phys., **18**, p. 766; 1907).

1. MAXWELL'S THEORY OF A HETEROGENEOUS DIELECTRIC

Maxwell has shown[10] that a *homogeneous* dielectric, even if its specific resistance be comparatively small, should be free from absorption. If, however, the dielectric be of *heterogenous* composition, absorption is a necessary consequence. Maxwell treated the case of a dielectric made up of parallel strata of different dielectrics and proved that unless the product, Kr, of the dielectric constant K and specific resistance r is the same for all the strata, charges will collect at the planes of contact of the various strata, which are only dissipated gradually on successive discharges of the condenser. That is, the composite dielectric shows the ordinary phenomenon of absorption. Maxwell confined his investigation to the case of a constant applied emf. Rowland[11] extended Maxwell's investigation to the case of a sinusoidal emf, and showed (*a*) that the capacity should depend upon the frequency, and (*b*) the phase difference between the current and the applied emf should differ from the ideal 90° existing in a homogeneous dielectric by an amount which is different according to the frequency. Rowland merely stated his results without proof. His equation for the equivalent resistance of the condenser seems to be slightly in error. The author has indicated the derivation of this result below:

Let the dielectric be considered as composed of parallel plane strata 1, 2, 3, ... of thicknesses a_1, a_2, a_3, ... dielectric constants K_1, K_2, K_3 ..... specific resistances r_1, r_2, r_3, ... and let the electric field strengths, assumed constant inside each stratum, be X_1, X_2, X_3, ...

The emf on the condenser is then

$$e = a_1 X_1 + a_2 X_2 + a_3 X_3 + \dots\dots$$

Maxwell's equations for the current density are

$$i = \frac{X_1}{r_1} + \frac{K_1}{4\pi}\frac{dX_1}{dt} = \frac{X_2}{r_2} + \frac{K_2}{4\pi}\frac{dX_2}{dt} = \dots\dots$$

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[10] Elect. and Mag., I, § 328–330.

[11] Scientific Papers, p. 297.

If we assume that the current obeys the sine law; that is, $i = I \sin pt$, where $p = 2\pi \times$ the frequency

$$I \sin pt = \frac{X_1}{r_1} + \frac{K_1}{4\pi}\frac{dX_1}{dt} = \frac{X_2}{r_2} + \frac{K_2}{4\pi}\frac{dX_2}{dt} = \ldots\ldots$$

The electric forces, therefore, satisfy the differential equation

$$\frac{dX}{dt} + \frac{4\pi}{Kr}X = \frac{4\pi}{K}I \sin pt.$$

The solution of this equation is

$$X = Ae^{-\frac{4\pi}{Kr}t} + \frac{\frac{(4\pi)^2}{K^2r}I}{p^2 + \left(\frac{4\pi}{Kr}\right)^2} \sin pt - \frac{4\pi pI}{K\left[p^2 + \left(\frac{4\pi}{Kr}\right)^2\right]} \cos pt.$$

The emf on the condenser is therefore

$$e = a_1A_1e^{-\frac{4\pi}{K_1r_1}t} + a_2A_2e^{-\frac{4\pi}{K_2r_2}t} + \ldots\ldots$$

$$+ (4\pi)^2I\left[\frac{a_1}{K_1^2r_1\left\{p^2 + \left(\frac{4\pi}{K_1r_1}\right)^2\right\}} + \frac{a_2}{K_2^2r_2\left\{p^2 + \left(\frac{4\pi}{K_2r_2}\right)^2\right\}} + \ldots\ldots\right]\sin pt$$

$$- 4\pi Ip\left[\frac{a_1}{K_1\left\{p^2 + \left(\frac{4\pi}{K_1r_1}\right)^2\right\}} + \frac{a_2}{K_2\left\{p^2 + \left(\frac{4\pi}{K_2r_2}\right)^2\right\}} + \ldots\ldots\right]\cos pt.$$

The exponential terms become neglible in a very short time, so that we have in the steady régime

$$e = \left(\frac{4\pi}{p}\right)^2 I\left[\frac{a_1}{K_1^2r_1\left\{1 + \left(\frac{4\pi}{K_1r_1p}\right)^2\right\}} + \frac{a_2}{K_2^2r_2\left\{1 + \left(\frac{4\pi}{K_2r_2p}\right)^2\right\}} + \ldots\ldots\right]\sin pt$$

$$- \frac{4\pi I}{p}\left[\frac{a_1}{K_1\left\{1 + \left(\frac{4\pi}{K_1r_1p}\right)^2\right\}} + \frac{a_2}{K_2\left\{1 + \left(\frac{4\pi}{K_2r_2p}\right)^2\right\}} + \ldots\right]\cos pt.$$

We may therefore write $e = E \sin (pt - \psi)$ where $E^2 = M^2 + N^2$ and $\tan \psi = \frac{N}{M}$, and N and M are respectively the coefficients of $\sin pt$ and $\cos pt$.

What we have designated as the *phase difference* is $\phi = 90° - \psi$ and is given by

$$\tan\phi = pC\rho = \frac{M}{N}$$

$$= \frac{4\pi}{p}\,\frac{\dfrac{a_1}{K_1^2 r_1\left\{1+\left(\dfrac{4\pi}{K_1 r_1 p}\right)^2\right\}}+\dfrac{a_2}{K_2^2 r_2\left\{1+\left(\dfrac{4\pi}{K_2 r_2 p}\right)^2\right\}}+\ldots}{\dfrac{a_1}{K_1\left\{1+\left(\dfrac{4\pi}{K_1 r_1 p}\right)^2\right\}}+\dfrac{a_2}{K_2\left\{1+\left(\dfrac{4\pi}{K_2 r_2 p}\right)^2\right\}}+\ldots .} \qquad (5)$$

where ρ is the equivalent resistance, in series with the capacity, which will produce this phase difference.

To find the capacity we remember that the component of the emf at 90° behind the current in phase is $\frac{I}{pC}$.

$$\therefore\ \frac{1}{C} = 4\pi\left[\frac{a_1}{K_1\left\{1+\left(\dfrac{4\pi}{K_1 r_1 p}\right)^2\right\}}+\frac{a_2}{K_2\left\{1+\left(\dfrac{4\pi}{K_1 r_1 p}\right)^2\right\}}+\ldots .\right]. \qquad (6)$$

For infinite frequency we obtain for the limiting value of the capacity C_o, unaffected by absorption

$$\frac{1}{C_o} = 4\pi\left[\frac{a_1}{K_1}+\frac{a_2}{K_2}+\ldots .\right]. \qquad (7)$$

This has frequently been designated as the *instantaneous* capacity. Curtis [12] uses the term *geometric capacity*, a name which has much to recommend it.

The equivalent resistance of the condenser ρ may be derived directly from equations (5) and (6), or we may derive its value from the energy loss in the condenser. The latter is found by integrating the product of the instantaneous current and the component of the emf in phase with the current, over the cycle. Placing this equal to $I_e^2\rho$, where I_e is the effective current, we find the same value for ρ as by the first method, viz:

$$\rho = \left(\frac{4\pi}{p}\right)^2\left[\frac{a_1}{K_1^2 r_1\left\{1+\left(\dfrac{4\pi}{pK_1 r_1}\right)^2\right\}}+\frac{a_2}{K_2^2 r_2\left\{1+\left(\dfrac{4\pi}{pK_2 r_2}\right)^2\right\}}+\ldots .\right]. \qquad (8)$$

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[12] This Bulletin, 6, p. 471; 1910.

If r_1, r_2, .. are large, as would naturally be expected to be the case, we may expand the equations (5), (6), and (8) in powers of $\frac{1}{p}$;

$$\frac{1}{C}=4\pi\left[\left(\frac{a_1}{K_1}+\frac{a_2}{K_2}+\ldots\right)-\left(\frac{4\pi}{p}\right)^2\left(\frac{a_1}{K_1^3r_1^2}+\frac{a_2}{K_2^3r_2^2}+\ldots\right)\right.$$

$$\left.+\left(\frac{4\pi}{p}\right)^4\left(\frac{a_1}{K_1^5r_1^4}+\frac{a_2}{K_2^5r_2^4}+\ldots\right)-\ldots\right] \quad (9)$$

$$\rho=\left(\frac{4\pi}{p}\right)^2\left(\frac{a_1}{K_1^2r_1}+\frac{a_2}{K_2^2r_2}+\ldots\right)-\left(\frac{4\pi}{p}\right)^4\left(\frac{a_1}{K_1^4r_1^3}+\frac{a_2}{K_2^4r_2^3}+\ldots\right)+\ldots \quad (10)$$

Rowland gave the same equation for $\frac{1}{C}$; his equation for ρ is

$$\rho=\frac{1}{p^2}\left[\frac{a_1}{r_1K_1^2}+\frac{a_2}{r_2K_2^2}+\ldots\right]-\frac{(4\pi)^2}{p^4}\left[\frac{a_1}{r_1^3K_1^4}+\frac{a_2}{r_2^3K_2^4}+\ldots\right]+\ldots$$

Hess[18] treated the special case of a pure capacity in series with a second capacity joined in parallel with a resistance. That is, he considered that an imperfect dielectric could be regarded as equivalent in its effect to a stratified dielectric, in which one of the two strata possesses an infinite specific resistance. He derived the equations for this case supposing a steady emf to be applied, and made experiments which seemed to support this theory.

It does not seem possible, on account of the number of variables involved, and the uncertainty as to how many and what kind of strata are present, to submit this theory to a quantitative test. *Qualitatively* there is, with a few possible exceptions, good agreement between the observations and the theory, as will next be shown.

With decreasing frequency, the capacity and phase difference should increase. The observations show, however, that the rate of increase is, in general, slower than would be demanded by only two terms in (5) and (6), unless r_1, r_2, .. are much smaller than would naturally be expected. It should, however, be possible, by assuming the number of strata large enough, to represent the observations. Curtis has shown in a recent article,[14] that assuming the dielectric of the mica condensers investigated by him to consist of a stratum of mica and a stratum of paraffin (used for sealing the condenser) and taking for the values of a_1, a_2, r_1, r_2 those found by direct measurement, the variation of the capacity and phase difference calculated from the above equations is much smaller than that actually found.

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[18] Lum. Elect., 46, p. 401, 507; 1892.

The curves connecting the capacity and phase difference with change of frequency are of the same general form for all of the condensers here investigated, the changes being more pronounced the greater the order of magnitude of the phase difference of the condenser. This can be reconciled with the assumption that r_1, r_2, . . are smaller in the condensers with the greater absorption. A consideration of the temperature curves is, however, more instructive.

The thicknesses of the strata a_1, a_2, . . . will in general increase with rising temperature. The coefficient of expansion of paraffin is known to increase rapidly as the temperature increases. The following values, taken from Landolt and Börnstein's tables, will illustrate this point:

Temperature	Average coefficient
0°–16°	0.00058
16°–38°	0.00070
38°–49°	0.00258
33°.5–37°.7	0.00260
37°.7–41.0°	0.00666

The capacity per unit area of the plates (to which the foregoing equations apply) should, therefore, as a result of the expansion of the paraffin, show a negative temperature coefficient, which should increase more and more rapidly as the temperature increases. On the other hand, the area of the sheets of the dielectric should increase with the temperature, thus tending to give a positive temperature coefficient, due to this cause. In most mica condensers which have been sealed with paraffin, and in the better paraffined paper condensers such as Mp, S_8, and S_{10}, the former effect predominates and the resultant temperature coefficient is negative, and becomes rapidly more negative with increasing temperature, in accordance with the change in thickness of the strata.

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[14] This Bulletin, 6, p. 474; 1910.

There seems to be a scarcity of data as to the effect of temperature changes on the dielectric constant. Mica has, according to Cassie [15] a small positive temperature coefficient. On this assumption, the effect of changes in the dielectric constant should be to give rise to a positive temperature coefficient of the capacity. It is possible that the very small positive temperature coefficients observed by Curtis [16] in mica condensers from which most of the paraffin had been squeezed out, and in silvered mica condensers generally, may be explained by a preponderance of this effect over that of changes of the thickness of the strata. This gains credibility from the fact that the capacity varies directly with the dielectric constant. Equation (5) shows that a positive temperature coefficient of the dielectric constant should give rise to a negative temperature coefficient of the phase difference. This assumes, however, that changes of r_1 and r_2 with the temperature are of less effect, which is not usually to be expected.

The magnitude of the specific resistances r_1, r_2, . . . is, however, according to this theory, perhaps the most important factor in the behavior of paraffined paper condensers. The temperature coefficient of insulation resistance is known to be negative, the value increasing rapidly with the temperature. Further, the temperature coefficient is, in general, greater for small values of r.

Bearing these points in mind, we are in a position to analyze the temperature curves of capacity and phase difference for the various condensers. Mp, S_8, and S_{10} may be considered as constituting one group. As already remarked, the temperature coefficients of their capacities are negative and nearly constant at the lower temperatures, but become rapidly more negative above about 25°. The condenser *Mp* has the largest coefficient, S_{10} the smallest. The effect of changes in $r_1, r_2, \ldots .$ is to tend to make the temperature coefficient positive, especially at the higher temperatures and lower frequencies. This effect is noticeable in S_8 and *Mp*. The phase difference of the latter is unusually small for a paper condenser, indicating relatively large values of the specific resistances, and consequently only small changes of phase difference with the temperature. In both cases, the tendency is for the temperature coefficient of the phase difference to change from negative, at the lower temperatures, to positive, at the higher frequencies, the temperature of the transition lying at a lower value, the lower the frequency. This can be explained, qualitatively at least, by the assumption that at the lower temperatures the effects of the decrease of capacity and increase of dielectric constant tending to cause a negative temperature coefficient of phase difference are together larger than the effect of the change in the specific resistances. As the temperature increases, the coefficients of $r_1, r_2, \ldots$ increase (more rapidly at the lower frequencies than at the higher), until the effect of the specific resistance preponderates. The phase difference is larger with S_8 than with *Mp*, indicating smaller values of the specific resistances in S_8 than in *Mp*. Consequently larger changes of the phase difference with the temperature would be expected in the former than in the latter, as was observed. The interpretation of the curves of S_{10} is difficult; it requires, perhaps, the assumption that in this condenser the temperature coefficient of the dielectric constant is more important than in the other two condensers. This would give rise to the relatively small temperature coefficient of the capacity, the effect being somewhat annulled at the lower frequencies, as already touched upon. This assumption finds support in the unusually large temperature coefficient of the phase difference, even at the lower frequencies, although the magnitude of the phase difference would lead one to anticipate as great effect of the specific resistance as with S_8.

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[15] Proc. Roy. Soc., 46, p. 357; 1889.

[16] This Bulletin, 6, p. 448; 1910.

The condensers *Cp*, *Lp*, $Be_{1,5}$, $Be_{3,4}$, t_3, t_{17} group themselves naturally in another class from those just considered. These are distinguished by positive temperature coefficients of capacity, the value of this coefficient increasing rapidly with the temperature, and with decreasing frequency. The phase difference curves are of the same character. The changes of both capacity and phase difference are on a much larger scale than those of the condensers already considered, and the actual magnitudes of the phase differences are in some cases excessive (compare those of t_3, t_{17}, $Be_{1,6}$, etc.).

According to the theory of a heterogeneous dielectric, the effect of the specific resistance, although in some of these cases nearly balanced at the lower temperatures and higher frequencies, must be the preponderating factor.

The drop in the phase difference curves of Cp at 30°–35°, and at the frequencies 33 and 100 is due to an actual permanent change taking place in the dielectric, which manifested itself by a permanent shift of the capacity curve at lower temperatures. In the curves of t_3, and, to a less extent, in those of t_{17}, the effect of the second term in the equation for ρ, which works in opposition to the main term, may perhaps be detected.

The remaining condensers partake, more or less, of both of the classes already discussed. *SH* shows very well the gradual change with the frequency of the factor which is predominant. The specific resistances of the strata are the principal factors in determining the temperature coefficient of the capacity. At 100 cycles the effect of the specific resistance is nearly balanced against that of the change in the thickness of the strata, the latter effect being the larger at the lower temperatures and the former at the higher. Finally, at 900 cycles the effect of the specific resistance has become so small that the curve has the distinctive shape of that produced by changes in the thicknesses of the strata alone. In the case of the phase differences the curves are what we would expect, the effect of the specific resistance being smallest at the highest frequency. The curves of S_6 are of the same nature as those of the preceding.

The condenser W_a is peculiar. It belongs to a lot of telephone condensers having the smallest phase difference (when corrected for internal resistance) of any telephone condensers yet tested by the author. The internal resistance of the plates is, however, large. The capacity temperature coefficient is positive and small (about 3 in 10 000). The bending of the curves in the region above 30° is to be attributed to a tendency of the capacity to become permanently lower at the higher temperatures. The phase difference changes but little with the temperature, but the observed curves taken in conjunction with the capacity curves, and the smallness of the value of the phase difference, perhaps indicates an unusually large influence of the dielectric constant.

Finally, the condenser T_2, which was markedly unstable at higher temperatures, resembles otherwise SH and S_6, although the effect of the specific resistance was larger with the latter condenser than with the former.

We thus see that *qualitatively* most of the peculiarities of all the observed curves may be explained by equations (5) and (6) in the light of assumptions which must, in the main, be qualitatively correct, although in some cases open to doubt. Undoubtedly the existence of heterogeneity in the dielectric gives rise to absorption, but whether this is even the *main* cause for the absorption is at least questionable. Several distinctive features of the curves of S_8, S_{10}, and Mp seem to point to the presence of other factors. In any case, the theory, in the light of our present knowledge, does not seem capable of quantitative proof.

2. HOULLEVIGUE'S THEORY OF FRICTIONAL RESISTANCE

In two articles entitled "Sur l'échauffement électrique des condensateurs" [17] and "Sur les theories du residu électrique" Houllevigue has elaborated Hopkinson's theory [18] of residual elasticity in terms of Maxwell's theory.

He assumes the displacement in an imperfect dielectric to consist of two parts—(*a*) an instantaneous displacement of the ether until the elastic forces between the ether and the molecules are in equilibrium and (*b*) an additional gradual yielding of the molecules under this tension, so that to the instantaneous displacement of the ether is added the displacement of the mean position of the molecules.

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[17] Jour. de Phys. (3), **6**, pp. 113 and 120; 1897.

[18] Phil. Trans., **167**, p. 599; 1877.

In viscous media the forces which determine the displacement depend not only on the magnitude of the displacement, but on the velocity with which it takes place; that is, there is a frictional reaction proportional to the velocity of the displacement which manifests itself in the heating observed in imperfect condensers. Houllevigue has formulated this theory both for the case of a steady and for a sinusoidal applied emf. His equations for the latter case, somewhat amplified and with several misprints corrected, are reproduced below.

(a) 1ST CASE. DIELECTRIC WITHOUT ABSORPTION

Let $\varDelta$ = the displacement at any moment of the ether
Φ = the field strength
ρ = the absolute density of the ether
e = the instantaneous difference of potential between the plates
d = the distance between the plates
S = the area of the plates
F = the elastic reaction of the ether, taken proportional to the displacement.

We have, then,

$$\Phi=\frac{e}{d}, \qquad F=\frac{4\pi}{K}\varDelta.$$

The displacement must satisfy, therefore, the differential equation

$$\rho\frac{d^2\varDelta}{dt^2}=\frac{e}{d}-\frac{4\pi}{K}\varDelta.$$

If the impressed emf is E_0 and the resistance and inductance of the external circuit are respectively R and L, then

$$E_0=e+Ri+L\frac{di}{dt}=e+RS\frac{d\varDelta}{dt}+LS\frac{d^2\varDelta}{dt^2}$$

where i, the current $=S\frac{d\varDelta}{dt}$, We have, therefore,

$$\left(L+\frac{\rho d}{S}\right)\frac{d^2\varDelta}{dt^2}+R\frac{d\varDelta}{dt}+\frac{4\pi d}{KS}\varDelta=\frac{E_0}{S}.$$

$\frac{\rho d}{S}$ will usually be neglible in comparison with L, and, remembering that $Q=S\varDelta$, $\frac{4\pi d}{KS}=\frac{1}{C}$, this is seen to be Thomson's classic equation. Putting $E_0=E\sin pt$, where $p=2\pi$ times the frequency and $L+\frac{\rho d}{S}=L'$, we have

$$L'\frac{d^2\varDelta}{dt^2}+R\frac{d\varDelta}{dt}+\frac{4\pi d}{KS}\varDelta=\frac{E}{S}\sin pt,$$

which gives

$$\varDelta=\frac{L'S(A^2+B^2)}{E}(A\sin pt-B\cos pt)+c_1e^{\alpha_1 t}+c_2e^{\alpha_2 t} \qquad (12)$$

where α_1 and α_2 are the roots of the equation $\alpha^2+\frac{R}{L'}\alpha+\frac{1}{L'C}=0$, and

$$A=\frac{1}{L'C}-p^2 \qquad B=p\frac{R}{L'} \qquad (13)$$

$C=\frac{KS}{4\pi d}$, the capacity of the condenser, and c_1, c_2 are constants.

Equation (12) gives for the steady régime

$$\varDelta=\frac{E}{pS\sqrt{R^2+\left(L'p-\frac{1}{pC}\right)^2}}\sin(pt+\theta)$$

$$\tan\theta=\frac{R}{pL'-\frac{1}{pC}} \qquad (14)$$

and

$$i=\frac{dQ}{dt}=S\frac{d\varDelta}{dt}=\frac{E}{\sqrt{R^2+\left(L'p-\frac{1}{pC}\right)^2}}\sin(pt+\varphi) \qquad (15)$$

$$\tan\varphi=\frac{\frac{1}{pC}-pL'}{R}$$

the usual equation for the current in a circuit containing resistance R, inductance L', and capacity C.

(b) 2ND. CASE, DIELECTRIC WITH ABSORPTION

In addition to the displacement Δ of the ether, we have here to assume a displacement Δ' of the molecules of the dielectric themselves. The forces acting on unit volume of the dielectric, are (*a*) the elastic force $\frac{4\pi\Delta}{K}$, due to the displacement Δ of the ether, (*b*) the elastic reaction $a\Delta'$ of the molecules, opposing the displacement of the molecules and proportional to it, (*c*) a frictional reaction $2b\frac{d\Delta'}{dt}$ proportional to the velocity of the molecules. Consequently, if P is the density of the dielectric,

$$P\frac{d^2\Delta'}{dt^2}=\frac{4\pi}{K}\Delta-a\Delta'-2b\frac{d\Delta'}{dt}. \tag{16}$$

To simplify the integration, and since we need not consider the external circuit, we put $R=0$, $L=0$, and insert for the displacement Δ its value

$$\Delta=\frac{E}{pS\left(p\frac{pd}{S}-\frac{1}{pC}\right)}\sin pt=\frac{E}{p^2pd-\frac{S}{C}}\sin pt$$
$$=A\sin pt.$$

The differential equation for Δ' becomes therefore,

$$\frac{d^2\Delta'}{dt^2}+\frac{2b}{P}\frac{d\Delta'}{dt}+\frac{a}{P}\Delta'=\frac{4\pi A}{KP}\sin pt$$

whose solution is

$$\Delta'=C_1e^{\beta_1 t}+C_2e^{\beta_2 t}+\frac{4\pi}{KP}A\,[M\sin pt+N\cos pt] \tag{17}$$

where β_1 and β_2 are the roots of the equation

$$\beta^2+\frac{2b}{P}\beta+\frac{a}{P}=0$$

$$M=\frac{\frac{a}{P}-p^2}{\left(\frac{a}{P}-p^2\right)^2+\frac{4b^2}{P^2}p^2} \tag{18}$$

$$N=-\frac{\frac{2b}{P}p}{\left(\frac{a}{P}-p^2\right)^2+\frac{4b^2}{P^2}p^2}$$

or in the steady state

$$\Delta'=A'\sin(pt+\theta)$$

where

$$A'=\frac{4\pi A}{KP}\frac{1}{\sqrt{\left(\frac{a}{P}-p^2\right)^2+\frac{4b^2}{P^2}p^2}}=Ax \tag{19}$$

$$\tan\theta=\frac{-\frac{2b}{P}p}{\left(\frac{a}{P}-p^2\right)}$$

The current is

$$\begin{aligned} i&=S\frac{d}{dt}(\Delta+\Delta') \\ &=SAp\,[\cos pt+x\cos(pt+\theta)] \\ &=SAp\,[(1+x\cos\theta)\cos pt-x\sin\theta\sin pt] \\ &=I\cos(pt-\varphi) \end{aligned}$$

where

$$I=SAp\sqrt{1+2x\cos\theta+x^2}$$

$$\tan\varphi=\frac{-x\sin\theta}{1+x\cos\theta}=\frac{\frac{4\pi}{KP}\cdot\frac{2bp}{P}}{\left(\frac{a}{P}-p^2\right)^2+\frac{4\pi}{KP}\left(\frac{a}{P}-p^2\right)+\frac{4b^2}{P^2}p^2} \tag{20}$$

The current in the case of the dielectric without absorption is $SAp\cos pt$. The increase in capacity ΔC due to absorption is therefore given by

$$\frac{\Delta C}{C}=x\cos\theta=\frac{4\pi}{KP}\,\frac{\left(\frac{a}{P}-p^2\right)}{\left(\frac{a}{P}-p^2\right)^2+\frac{4b^2}{P^2}p^2} \tag{21}$$

and the phase difference is equal to the angle φ just derived. From the equation

$$\beta^2+\frac{2b}{P}\beta+\frac{a}{P}=0,$$

we have

$$\beta=-\frac{b}{P}\pm\sqrt{\frac{b^2}{P^2}-\frac{a}{P}}$$

Excluding therefore the case of an oscillatory charge, β will be real and negative and $\frac{b^2}{P^2}>\frac{a}{P}$. The term $\frac{4\pi}{KP}$ will vary for different dielectrics.

An interesting consequence of the equation (21) for $\frac{\Delta C}{C}$ is that with indefinitely increasing frequency, ΔC must at length change sign and the capacity become less than the value of the capacity as unaffected by absorption, i. e., the geometrical capacity, and with still greater frequency, approach asymptotically the geometrical capacity.

The physical significance of the equations (20) and (21) may be seen from the following considerations. The quantity $\frac{a}{P}$ is equal to $4\pi^2/T^2$, where T is the natural period of vibration of the molecules, when acted on by the elastic reaction alone, friction being supposed negligible. Equations (19) show that the phase of the viscous displacement lags behind that of the applied electric field by an angle which increases with increasing frequency, and which is greater the greater the frictional resistance to the displacement of the molecules. When the frequency reaches a value equal to that of the natural frequency of vibration of the molecules under the elastic restoring forces $\left(\frac{a}{P}=p^2\right)$ equation (19) shows that the viscous displacement Δ' lags behind the field by exactly 90°; the energy is all expended in supplying the frictional losses, and the amplitude of vibration is the same as would be the case in a perfect dielectric, since there is no component of the viscous displacement in phase with the field.

When $\left(\frac{a}{P} \gtrless p^2\right)$ the viscous displacement may be decomposed into two components, one in phase with the field, and the other at right angles with it. The latter is the component which overcomes the friction, while the former increases the ideal displacement or is subtracted from it according as $\frac{a}{P}$ is less than or greater than p^2.

There is no experimental evidence in support of such a law of change of capacity with the frequency.

From the nature of the observed curves of capacity, and from the fact that Curtis found good agreement between the limiting value of the capacity, with increasing frequency, as extrapolated both from direct current and alternating current measurements, it does not seem reasonable to suppose that (21) actually represents the facts. If, however, it is ever found that with increasing frequency the capacity reaches a certain minimum value, and then rises slowly to a limiting value, this very simple theory will receive a valuable support.

Beyond the condition $\frac{b^2}{P^2} > \frac{a}{P}$, the values of the constants in the formula (21) are unrestricted, but notwithstanding this freedom of choice of their values the observations do not appear to follow the law in question.

3. PELLAT'S THEORY

Pellat assumed[19] that, when a field of strength E_0 is impressed on a dielectric, the displacement instantaneously takes up the value $D = \frac{K}{4\pi}E_0$, where K is the dielectric constant, and then increases logarithmically toward a final value $(1+\epsilon)$ times as great,

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[19] Ann. Chim. et Phys., 18, p. 150; 1899.

ϵ being small compared with unity. That is

$$D_t = \frac{K}{4\pi} E_0 \left[1 + (1 - e^{-\alpha t})\epsilon\right] \tag{22}$$

and therefore

$$D_\infty = \frac{K}{4\pi} E_0 (1 + \epsilon).$$

Accordingly

$$\frac{dD_t}{dt} = \alpha e^{-\alpha t} \frac{\epsilon K E_0}{4\pi} = \alpha(D_\infty - D_t). \tag{23}$$

That is, the rate of increase of the displacement at any moment is proportional to the difference between the final value and that existing at the time in question. Such a law has been advocated by several different observers from work with direct currents. The following extension of this theory to the case of a sinusoidal emf is adapted from von Schweidler's valuable and comprehensive article on dielectric theory.[20]

For any law of variation of the electric force with the frequency $E_t = f(t)$,

$$D_t = \frac{KE_t}{4\pi} + D_t' \tag{24}$$

where the instantaneous displacement D'_t is subject to the relation

$$\frac{dD_t'}{dt} = \alpha(D_\infty - D_t) \tag{25}$$

D_∞ being the final value of the displacement which would be reached if the electric field were held constant at the instantaneous value E_t.

But from (22)

$$D_\infty = \frac{K}{4\pi} E_t \, (1 + \epsilon)$$

and hence and from (24) and (25)

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[20] Ann. der Phys., **24**, p. 711; 1907.

$$\frac{dD_t'}{dt}=\alpha\left[\frac{K\epsilon}{4\pi}E_t-D_t'\right]$$

or

$$\frac{dD_t'}{dt}+\alpha D_t'=\frac{\alpha K\epsilon}{4\pi}E_t. \qquad (26)$$

Assuming now $E_t=E_0 \sin pt$

$$\frac{dDt'}{dt}+\alpha D_t'=\frac{K\alpha\epsilon}{4\pi}E_0 \sin pt \qquad (27)$$

whose solution is

$$D_t'=Ae^{-\alpha t}+M \sin pt+N \cos pt$$

where

$$M=\frac{\alpha^2\epsilon KE_0}{4\pi(p^2+\alpha^2)}$$

$$N=-\frac{\alpha p\epsilon KE_0}{4\pi(p^2+\alpha^2)}. \qquad (28)$$

The current is

$$i=\frac{dD_t}{dt}=\frac{K}{4\pi}\frac{dE_t}{dt}+\frac{dD_t'}{dt}$$

$$=\frac{pKE_0}{4\pi}\cos pt+\frac{dD_t'}{dt}$$

or in the steady régime

$$i=\frac{KE_0p}{4\pi}\left(1+\frac{\alpha^2\epsilon}{p^2+\alpha^2}\right)\cos pt+\frac{KE_0}{4\pi}\left(\frac{p^2\alpha\epsilon}{p^2+\alpha^2}\right)\sin pt \qquad (29)$$

or

$$i=I\cos(pt-\varphi)$$

where

$$\tan\varphi=\frac{\dfrac{p^2\alpha\epsilon}{p^2+\alpha^2}}{p\left(1+\dfrac{\alpha^2\epsilon}{p^2+\alpha^2}\right)}=\frac{\alpha\epsilon p}{p^2+\alpha^2(1+\epsilon)} \qquad (30)$$

$$I=\frac{KE_0}{4\pi}\,\frac{p^2}{p^2+\alpha^2}\sqrt{\left\{1+\frac{\alpha^2}{p^2}(1+\epsilon)\right\}^2+\alpha^2\epsilon^2}$$

Since the emf is in phase with the electric field, φ is the *phase difference.*

The current in a condenser without absorption, acted upon by a sinusoidal emf is, as we have seen, $\frac{dD_t}{dt}=\frac{KE_0p}{4\pi}\cos pt$. We find accordingly that

$$\frac{\Delta C}{C}=\frac{\alpha^2\epsilon}{p^2+\alpha^2} \tag{31}$$

These simple equations are not satisfied by the observations of this paper, and were also found insufficient by von Schweidler.

4. MODIFIED PELLAT THEORY OF VON SCHWEIDLER

Having found that the Pellat theory, although in qualitative agreement with the observed phenomena in dielectrics, did not represent his measurements quantitatively, von Schweidler went a step further, and made the assumption that the law of change of the absorbed charge, instead of being expressed by a single exponential term as in Pellat's theory, may be represented by a series of such terms, viz:

$$D_t=\frac{KE_0}{4\pi}\left[1+\Sigma\epsilon(1-e^{-\alpha t})\right]$$

and that as a consequence

$$\frac{\Delta C}{C}=\frac{\alpha_1^2\epsilon_1}{p^2+\alpha_1^2}+\frac{\alpha_2^2\epsilon_1}{p^2+\alpha_2^2}+\frac{\alpha_3^2\epsilon_3}{p^2+\alpha_3^2}+\dots. \tag{32}$$

$$\tan\varphi=\frac{\alpha_1\epsilon_1p}{p^2+\alpha_1^2(1+\epsilon_1)}+\frac{\alpha_2\epsilon_2p}{p^2+\alpha_2^2(1+\epsilon_2)}+\dots. \tag{33}$$

In its greatest generality the number of these terms may be supposed infinite, the constants α_t having values varying continuously between 0 and ∞. The factors ϵ_t corresponding will be functions of α, $f(\alpha)$, so that we may write

$$D_t=\frac{KE_0}{4\pi}\left[1+\int_0^\infty f(\alpha)\{1-e^{-\alpha t}\}d\alpha\right]$$

and consequently

$$\frac{\Delta C}{C} = \int_0^\infty \frac{\alpha^2 f(\alpha)}{p^2+\alpha^2} d\alpha \tag{34}$$

$$\tan \varphi = \int_0^\infty \frac{\alpha p f(\alpha)}{p^2+\alpha^2\{1+f(\alpha)\}} d\alpha \tag{35}$$

The function $f(\alpha)$ being determined from the observations. Viewed mathematically von Schweidler has thus introduced into Pellat's equation for the change of displacement with the time, a sufficient number of constants to represent the complicated empirical function derived from the observations. To meet the objection that this may appear as nothing more than "an artificial, purely mathematical fiction," von Schweidler goes on to show that his assumption is capable of a simple physical interpretation. This exposition of his theory is given so clearly and concisely by von Schweidler[21] that it has seemed well to reproduce a translation of the same at length below. He says.

> The molecules, which according to the electron theory consist of complexes of ions, may be regarded as resonators, in that the ions when displaced from their equilibrium positions possess definite natural periods of vibration. The phenomena of normal and abnormal dispersion of electric waves, together with the accompanying phenomena of absorption, are treated from this standpoint in the modern theory.
>
> In addition, now, to molecules whose ions possess a definite period of vibration and a definite damping, we may suppose others to be present whose damping is so great that, instead of oscillating, their motion is *aperiodically damped*. Under the influence of a suddenly applied constant electric field these approach a new equilibrium position in such a way that their deviation from the latter diminishes as the exponential function $e^{-\alpha t}$.
>
> The molecular-physical signification of the Pellat theory is, according to this point of view, as follows: In addition to those molecules which as resonators of definite (very small) period of oscillation follow the relatively slowly changing electric fields without an appreciable difference of phase, there are also present in an anomalous dielectric still other molecules in which the displacement of the ions takes place aperiodically damped, the constant α of the above formula having the same value for all the molecules. The quantity ϵ shows in what ratio the flux of the displacement of these aperiodically damped molecules stands to that of the molecules whose motion is oscillatory.
>
> In the modified theory the assumption is made that not only *one* kind of such aperiodically damped complexes of ions with a definite time constant α is present, but on the contrary that a large number of different kinds having different time con-

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[21] Ann. der Phys., **24**, pp. 747–748; 1907.

stants α_i are concerned, the number per unit volume of each kind being proportional to the quantity ϵ_i.

Going a step further, the possible values of the damping may be regarded as varying continuously, and the function $\epsilon = f(\alpha)$ shows according to what law these molecules are distributed as α varies continuously between 0 and ∞.

The decomposition of an empirically given function into a sum of simple exponential functions corresponds then physically to a separation of the effects which are produced by different groups of molecules of the same kind.

To completely determine the distribution ϵ of the aperiodically damped molecules as a function of the time constant α—that is, to determine the form of $f(\alpha)$ in the equations (34) and (35) from the observed curves of $\frac{\Delta C}{C}$ and tan φ is probably impossible, and von Schweidler seems to have made no comparison of his results (found with steady currents) with the theory just exposed. It appeared worth while, however, to the author of the present paper to attempt to determine a finite number of constants in the formulas (34) and (35), and the results obtained show the adequacy of a few terms of the modified Pellat theory to represent empirically the observations of this paper. Before giving the constants thus found for some of the condensers here studied we will consider more closely the method used in calculating the α's and ϵ's.

(a) METHOD OF CALCULATING THE CONSTANTS

We are met at the start with the difficulty that the capacity curves do not give us $\frac{\Delta C}{C}$ directly, since the limiting or geometrical capacity is not known. The first method which suggests itself is to calculate $\alpha_1, \alpha_2, \alpha_3, \ldots$ and $\epsilon_1, \epsilon_2, \epsilon_3, \ldots$ from the curve of the change of phase difference with the frequency, the $2n$ unknowns being determined from the $2n$ simultaneous equations formed from the $2n$ measured ordinates of the curve. The form of these equations is, however, too complicated to make this practically feasible even if these curves were free from the effect of internal resistance. The capacity-frequency curves give us the *differences* in the quantity $\frac{\Delta C}{C}$ with different frequencies, but the equations connecting these observed values with the α's and ϵ's are not simple enough to render hopeful the solution of the simultaneous equations formed from these observations.

The problem appears to be incapable of an exact solution without at least prohibitive labor. A number of methods for obtaining an approximate solution were tried, with the result that it seems best to assume, first, probable values of the α's and then to solve for the ϵ's from the capacity curves. The values found are then used to calculate the phase differences at varying frequencies, and the curve thus derived is compared with the observed curve. If necessary, the α's are corrected by trial and the solution repeated until the calculated values of the phase difference are in sufficiently good agreement with those observed.

In the scheme finally adopted the ordinates of the capacity curve were measured at the frequencies 33⅓, 100, 300, and 900 cycles. From these the *differences* in the quantity $\frac{\Delta C}{C}$ is obtained for the frequency intervals 33⅓–100, 100–300, and 300–900, thus giving three values δ_1, δ_2, δ_3. Now, supposing for the moment that we have only one term in the equation (32) for $\frac{\Delta C}{C}$ we find for frequencies corresponding to values p, ap, a^2p, and a^3p

$$\frac{\Delta_1 C}{C} = \frac{\alpha^2\epsilon}{p^2+\alpha^2} = \frac{\epsilon}{1+\frac{1}{x^2}}, \quad \frac{\Delta_3 C}{C} = \frac{\alpha^2\epsilon}{a^4p^2+\alpha^2} = \frac{\epsilon}{1+\frac{a^4}{x^2}}$$

$$\frac{\Delta_2 C}{C} = \frac{\alpha^2\epsilon}{a^2p^2+\alpha^2} = \frac{\epsilon}{1+\frac{a^2}{x^2}} =, \quad \frac{\Delta_4 C}{C} = \frac{\alpha^2\epsilon}{a^6p^2+\alpha^2} = \frac{\epsilon}{1+\frac{a^6}{x^2}}$$

where $x = \frac{\alpha}{p}$. Therefore using only one term

$$\delta_1 = \epsilon\left(\frac{1}{1+\frac{1}{x^2}} - \frac{1}{1+\frac{a^2}{x^2}}\right) = D\epsilon$$

$$\delta_2 = \epsilon\left(\frac{1}{1+\frac{a^2}{x^2}} - \frac{1}{1+\frac{a^4}{x^2}}\right) = D'\epsilon \qquad (37)$$

$$\delta_3 = \epsilon\left(\frac{1}{1+\frac{a^4}{x^2}} - \frac{1}{1+\frac{a^6}{x^2}}\right) = D''\epsilon.$$

In the actual case chosen we may consequently write:

$$\begin{aligned} \delta_1 &= D_1\epsilon_1 + D_2\epsilon_2 + D_3\epsilon_3 \\ \delta_2 &= D_1'\epsilon_1 + D_2'\epsilon_2 + D_3'\epsilon_3 \\ \delta_3 &= D_1''\epsilon_1 + D_2''\epsilon_2 + D_3''\epsilon_3 \end{aligned} \tag{38}$$

where the quantities D_1, D_2, D_3 are found from D by giving to x the successive values $x_1 = \frac{\alpha_1}{p}$, $x_2 = \frac{\alpha_2}{p}$, etc., and similarly the coefficients D_1', D_2', D_3'' and D_1'', D_2'', D_3'' are derived from D' and D''. These coefficients may be calculated and tabulated for various values of the x's, and such a table has been found to expedite the work greatly.

Having now assumed certain values of the α's, and therefore for the x's, we write out the equations (38), taking the coefficients D from the table, and solve for the values of ϵ_1, ϵ_2, and ϵ_3.

The phase differences φ_1, φ_2, φ_3, and φ_4 corresponding to the frequencies 33⅓, 100, 300, and 900 cycles may then be calculated from the equations

$$\begin{aligned} \tan\varphi_1 &= \frac{x_1\epsilon_1}{1+x_1^2(1+\epsilon_1)} + \frac{3x_2\epsilon_2}{1+9x_2^2(1+\epsilon_2)} + \frac{9x_3\epsilon_3}{1+81x_3^2(1+\epsilon_3)} \\ \tan\varphi_2 &= \frac{3x_1\epsilon_1}{9+x_1^2(1+\epsilon_1)} + \frac{x_2\epsilon_2}{1+x_2^2(1+\epsilon_2)} + \frac{3x_3\epsilon_3}{1+9x_3^2(1+\epsilon_3)} \\ \tan\varphi_3 &= \frac{9x_1\epsilon_1}{81+x_1^2(1+\epsilon_1)} + \frac{3x_2\epsilon_2}{9+x_2^2(1+\epsilon_2)} + \frac{x_3\epsilon_3}{1+x_3^2(1+\epsilon_3)} \\ \tan\varphi_4 &= \frac{27x_1\epsilon_1}{729+x_1^2(1+\epsilon_1)} + \frac{9x_2\epsilon_2}{81+x_2^2(1+\epsilon_2)} + \frac{3x_3\epsilon_3}{9+x_3^2(1+\epsilon_3)}. \end{aligned} \tag{39}$$

In all cases except for condensers of large absorption it will be found that the ϵ's are small with respect to unity, so that tables may be formed of the coefficients $\frac{x_1}{1+x_1^2}$, $\frac{3x_2}{1+9x_2^2}$, etc., corresponding to different values of α_1, α_2, and α_3 with a consequent saving of time.

The whole difficulty lies in the determination of the α's. A rough approximation to their values may be obtained from the capacity-frequency curves, on the assumption that the change of capacity at each point is represented principally by the changes of a single term in the expression (32) for $\frac{\Delta C}{C}$. For example, we may assume that the shape of the curve near 33⅓ cycles is mainly dependent on the value of α_1 alone, the shape near 100 cycles on α_2 alone, etc. Measuring ordinates at frequencies corresponding to p, ap, and bp, we find from the curve their differences.

$$\delta_0 = \frac{x^2(a^2-1)}{(1+x^2)(a^2+x^2)}\epsilon\,,\quad \delta_0' = \frac{x^2(b^2-a^2)}{(a^2+x^2)(b^2+x^2)}\epsilon$$

and

$$z = \frac{\delta_0}{\delta_0'} = \frac{a^2-1}{b^2-a^2}\;\frac{b^2+x^2}{1+x^2}.$$

Therefore

$$x^2 = \frac{\alpha^2}{p^2} = \frac{Mb^2-z}{\zeta-M}$$

where

$$M = \frac{a^2-1}{b^2-a^2}$$

On applying this process to the curves of this paper, it was found that the underlying assumption is only in a general way true. Fortunately, excepting for the value of the smallest time constants α_1, quite extensive changes in the α's produce relatively small changes in the calculated values of the phase differences. In the single instance of α_1, the rough values found by the above method from the capacity-frequency curve are invariably too large to give the observed value of the phase difference at the smallest frequency, 33 cycles. This is explained by the fact that the character of the capacity curve is changing so rapidly in this region of frequencies that if intervals of frequency be selected large enough to carry through the method already described, the value found corresponds to an actual frequency so much larger than that for which the value of α_1 is required that the calculated value is not applicable. It also appears that the curve of phase difference at the lower frequencies is more sensitive to changes in the value selected for α_1 than is the capacity curve. The natural suggestion that the α's should be calculated from the shape of the phase difference curve did not prove to be of advantage, since the phase difference curve, in addition to the errors of its determination, is subject to an uncertain error due to the internal resistance of the condenser, as already pointed out (p. 517).

The determination of the constants reduces, therefore, to a process of cut and try. The α's were obtained roughly, as already described, from the capacity curve, the simultaneous equations for the ϵ's written down in terms of these values of the α's, and solved for ϵ_1, ϵ_2, and ϵ_3. The phase difference curve corresponding to this first approximation was usually found to fit the observed curve very well excepting at the lower frequencies, where it was occasionally as much as 20 per cent in error. Assuming for ϵ_2 and ϵ_3 the values just found, an equation involving ϵ_1 and α_1 alone may be written down, both for the change of capacity and for $\tan \varphi_1$. Different values of α_1 are then assumed, the values of ϵ_1 corresponding calculated, and thence φ_1. By interpolation a value of α_1 is quickly obtained which satisfies both curves, and with this value the solution for ϵ_1 ϵ_2, ϵ_3, is repeated. It is in some cases found necessary to slightly change the values of α_2 and α_3 to fit the observations a little more exactly. This method is applicable to the determination of a greater number of constants, so that the calculated curve may pass through a greater number of observed points. Several curves were thus treated, and values of $\epsilon_1, \epsilon_2, \epsilon_3, \ldots \epsilon_6$ and $\alpha_1, \alpha_2, \alpha_3, \ldots . \alpha_6$ obtained. No further light on the behavior of the condensers was, however, thus obtained, and the difficulties of the solution of the problem are much increased.

(b) CALCULATED RESULTS

In Table IV are given the results of the calculation of the constants of a number of the condenser curves.

In the third and fourth columns of the table are given the values of the constants α and ϵ for the various condensers. In the fifth column are the values of the phase difference, calculated therefrom, and in the sixth column the values observed. The differences between the observed and computed values, given in the seventh column, are roughly proportional to the frequency, and

TABLE IV

Condenser	Temp.	α	ϵ	φ calc.	φ obs.	Diff.	Freq.	$\frac{\Delta C}{C}$ calc
	°			"	"	"		
S_8	15	132	0.00575	695	720	28	$33\frac{1}{3}$	0.00784
		770	.00171	627	690	63	100	
		2660	.00463	656	850	194	300	
				444	830	386	900	.00087
S_8	35	42	.02925	1366	1380	14	$33\frac{1}{3}$	.00628
		487	.00186	773	1015	242	100	
		2310	.00361	592	835	243	300	
				338	756	418	900	.00052
Mp	15	150	.00268	364	364	0	$33\frac{1}{3}$	.00431
		1090	.00256	384	384	0	100	
		3260	.00096	357	450	94	300	
				198	450	252	900	.00033
Mp	25	187	.00285	380	380	0	$33\frac{1}{3}$	.00500
		674	.00098	368	384	16	100	
		3260	.00284	376	403	27	300	
				298	426	128	900	.00073
S_{10}	15	209	.00369	541	555	14	$33\frac{1}{3}$	.00911
		888	.00185	619	656	37	100	
		3260	.00553	725	972	247	300	
				582	1084	452	900	.00143
S_{10}	35	45	.00935	578	588	10	$33\frac{1}{3}$	.00545
		562	.00188	475	534	59	100	
		3260	.00378	489	590	101	300	
				390	677	287	900	.00096
B	20	94	.00105	103	105	2	$33\frac{1}{3}$	.00084
		888	.00039	80	80	0	100	
		3260	.00029	68	63	—5	300	
				42	44	2	900	008.00
				° '	° '	'		
t_{17}	15	102	.1768	4 28	4 30	2	$33\frac{1}{3}$	.0926
		628	.0274	2 34	3 00	26	100	
		2660	.0341	1 50	2 32	42	300	
				1 04	2 03	59	900	.0065
t_{17}	35	98	.449	12 7	12 12	5	$33\frac{1}{3}$	.2682
		445	.1344	7 28	7 42	14	100	
		1884	.0780	4 36	5 04	28	300	
				2 05	3 41	96	900	.0087

the values of the internal resistance calculated from the differences are in fair agreement, in the majority of the cases, with those obtained by the other method above. Whereas, in that instance, it was assumed that the curves of phase difference should fall with the increasing frequency, these calculations show that this assumption is subject to some modification with Mp and S_{10}, and the observed curves show apparent anomalies which are in agreement with the calculated form of curve.

In the ninth column are calculated the differences between the observed capacity and the geometrical capacity in terms of the latter. These are found by substituting the calculated values of the α's and ϵ's in the equation (32) for $\frac{\Delta C}{C}$. It may be objected that this extrapolated value is open to doubt. It is, however, true in every instance that the capacity falls only slowly above 1000 cycles, and Curtis[22] has shown that the capacity extrapolated over the range of periods between 0.001 second and zero is in good agreement with the value extrapolated from the curve of capacity with different discharge periods and with steady current.

It is, further, a fact that the geometrical capacity thus derived is not very largely dependent on quite considerable errors in the constants α_2 and α_3, on which it rests. It seems, therefore, probable that the value of the geometrical capacity thus calculated is at least a fair approximation to the correct value, and in lieu of accurate methods for the direct determination of this important quantity, this method has much to recommend it.

An examination of the relations between the various constants of the condensers enables us to draw some important conclusions regarding the observed curves in the light of the modified Pellat theory.

(c) DISCUSSION OF OBSERVATIONS IN THE LIGHT OF THIS THEORY

The condenser t_{17} is, we have seen, typical of a class of condensers which includes Cp, Lp, $Be_{1,5}$, Be_{24}, and t_2. In all of these molecules are present whose time constants $\frac{1}{\alpha}$ cover a wide range of values. Although the number present is large with both large and small values of α, those with strong damping (large time constant) predominate. As the temperature rises the number of aperiodically damped molecules of all degrees of damping increases rapidly, but at a greater rate in the case of the small values of α (strong damping) than for the more feebly damped. As a consequence the phase difference rises with the temperature, and most rapidly at the lower frequencies.

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[22] This Bulletin, 6, p. 482; 1910.

The behavior of the better condensers is not simple, although it is satisfactorily explained by the modified Pellat theory. With Mp, for example, the number of aperiodically damped molecules is small at the observed temperatures. At 15° the number is largest with small and medium values of α. As the temperature rises to 25° the feebly damped molecules increase more rapidly in number than those with small values of α. The sum total of aperiodically damped molecules is not, however, very different at the two temperatures, which gives an explanation of the fact that the phase difference remains nearly constant over this range of temperature, except at the higher frequencies, where the increase of the number of feebly damped molecules has its greatest effect in changing the phase difference. Another result of this peculiar change in the distribution of the molecules is to give a greater capacity, relatively to the geometrical value, for a frequency of 900 cycles, at 25° than at 15°. Unfortunately the enormous temperature coefficient of the capacity of this condenser in the neighborhood of 35°, taken in connection with the uncertainties in the measurement of the temperature in this region (see p. 509) prevented a trustworthy determination of the constants in the case of the curve at 35°.

In the case of S_{10} at 15° the number of molecules of small time constant are actually more numerous than those of large time constant, and the phase difference increases with increasing frequency until 300 cycles is reached, after which it begins to fall off as in the usual run of condensers. As the temperature is raised, however, the number of strongly damped molecules rapidly increases, while at the same time those with small damping become less numerous, so that at 35° we have the nearly normal curve of phase difference, except that its fall with the frequency is a little retarded in the region of from 100 to 300 cycles. The capacity of this condenser relatively to the geometrical capacity is unlike that of *Mp*, larger at 15° and a frequency of 900 per second than at 25° and the same frequency.

The facts are with S_8 very much the same as in the preceding case, except that at 15° the feebly damped molecules, although numerous, are overbalanced by those which are strongly damped. At 35° the number of feebly damped molecules has appreciably decreased, causing a decrease of capacity at 900 cycles (relatively to the geometrical capacity at the temperature in question) in going from 15° to 35°. The phase difference curve at 35° is of quite the usual form.

The constants of the mica condenser *B* are appended for comparison. The calculated curve of phase difference fits the observed very exactly over the whole range of frequency, indicating that the internal resistance of the condenser taken in connection with its small capacity (0.1 mf) is not large enough to appreciably affect the measured values of the phase difference.

From what has gone before, we see, therefore, that all the peculiarities of the observed curves may be accounted for by the theory with the aid of quite natural assumptions. The nature of the phenomena taking place in an imperfect dielectric are summarized thus:

In a perfect dielectric the molecules (by which name we will designate complexes of ions in general) which have very high frequencies of vibration and small damping are in continual vibration, but their equilibrium positions follow the relatively slow changes of the applied electric field without sensible retardation.

If, due to some cause, molecules be present whose motion is aperiodically damped, the displacements of these anomalous molecules will lag in phase behind the changes of the field, giving rise to a loss of energy in the dielectric, and an increase in the effective value of the capacity of the condenser. The dielectric is to be regarded as imperfect.

In a nearly perfect dielectric the number of these aperiodically damped molecules will be small, and their damping will be feeble.

The distribution of these anomalous molecules as a function of the damping will vary with different condensers. In general it may be said that the greater the proportion of the molecules of feeble damping the more important the absorption effects at high frequency, the effects of the molecules of strong damping being more pronounced at the lower frequencies.

We have thus the case of relatively good condensers—few anomalous molecules, with relatively small damping. In the mica condenser *B* these molecules are distributed over a large range of damping, those of strong damping being predominant, but the number present of all degrees of damping is small. The condition of affairs with the condenser *Mp* at the lower temperature is much the same, only the number of anomalous molecules present is larger than with the mica condenser. With S_8 and S_{10} the proportion of feebly damped molecules is larger, as is also the total number present of all degrees of damping.

As the temperature rises the tendency in all these better paper condensers is for the proportion of the feebly damped molecules to increase to a maximum while the sum total changes but slowly. (See *Mp*.) When, however, this maximum has been reached, the number of strongly damped molecules becomes increasingly important. (See S_8 and S_{10}.)

With increasing temperature a point is at length reached where the total number of aperiodically damped molecules is very appreciable, those of strong damping being present in the largest proportions, and not only does the total number increase as the temperature rises still further, but the relative increase is larger with the strongly damped than with the feebly damped molecules. This last phase, which is illustrated by the better condensers at relatively high temperatures, is characteristic of the poorer condensers at room temperatures. There is experimental evidence to lead to the belief that at sufficiently low temperatures these latter condensers would also behave like the condensers *Mp*, S_8, S_{10}, etc.

5. HOPKINSON'S THEORY OF ELASTIC AFTER EFFECT

In 1876 Hopkinson advanced the theory that the phenomena of absorption owe their origin to strains in the medium which persist after the removal of the cause which gives rise to them. This idea, which was suggested to him by Maxwell, Hopkinson treats in a manner similar to that adopted by Boltzmann[23] in 1874 in the developement of the theory of the after effects of mechanical strain.

If θ_t be the angle of torsion of a wire at the time t, the couple acting is not only proportional to this angle but previous strains have also an effect. The effect of an angle of torsion $\theta_{t-\omega}$ at a time ω seconds previous will depend on the angle of torsion, the length of time during which it persisted, $d\omega$, and decays with the time in the manner given by some function $f(\omega)$ of the interval which has elapsed up to the time t under consideration.

The torque L is therefore given by the equation

$$L = a\theta_t - \int_0^\infty \theta_{t-\omega} f(\omega) d\omega$$

By analogy Hopkinson wrote, therefore,

$$x_t = y_t - \int_0^\infty y_{t-\omega} \varphi(\omega) d\omega \tag{40}$$

where x_t = the potential between the terminals at the time t and y_t = the surface integral of the displacement, divided by the geometrical capacity, and he then went on to apply this equation to his measurements with a steady applied electromotive force.

Let us now adapt this hypothesis to the case of alternating currents. In an ideal dielectric the displacement is given by $D = \frac{E_0 K}{4\pi} \sin pt$, where E_0 is the amplitude of the electric field. The actual displacement in the imperfect dielectric is greater by an amount D', which is the integral of the residual displacements, due to the previous values of the applied emf. At any time τ seconds previous to the time under consideration, the emf. existing at that time would produce an residual effect proportional to its value $E_0 \sin p\ (t-\tau)$, and to the time $d\tau$ during which it was applied, and this displacement would fall off according to some function of the elapsed time τ. We can write therefore

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[23] Wien. Ber. II, 70, Oct., 1874.

$$D' = \int_0^\infty \frac{E_0K}{4\pi} \sin p(t-\tau) \, . f(\tau)d\tau.$$

If we now make the assumption that the residual displacements decay according to a simple exponential law, and set $f(\tau) = \alpha\epsilon e^{-\alpha\tau}$ we find, remembering that

$$\int_0^\infty e^{-\alpha\tau} \sin p(t-\tau)d\tau = \int_{-\infty}^{t} e^{-\alpha t}e^{\alpha T} \sin pTdT$$

the total displacement D will be given by

$$D = \frac{E_0K}{4\pi} \sin pt + \frac{E_0K}{4\pi}\alpha\epsilon\left[\frac{\alpha \sin pt - p \cos pt}{p^2+\alpha^2}\right]$$

The current i may be found at once

$$i = \frac{dD}{dt} = \frac{pKE_0}{4\pi}\left[\left(1 + \frac{\alpha^2\epsilon}{p^2+\alpha^2}\right)\cos pt + \frac{\alpha\epsilon p}{p^2+\alpha^2}\sin pt\right]$$

from which the capacity C' is given in terms of the geometrical capacity C_0 by the relation

$$C' = C_0\left[1 + \frac{\alpha^2\epsilon}{p^2+\alpha^2}\right]$$

and the phase difference is

$$\tan \varphi = \frac{\alpha\epsilon p}{p^2+\alpha^2(1+\epsilon)}$$

These are seen to be Pellat's equations, as applied to alternating currents, and if instead we had assumed a steady applied electromotive force we would have found for the displacement

$$D = \frac{E_0K}{4\pi}[1 + \epsilon(1 - e^{-\alpha t})]$$

which is Pellat's initial equation (22).

According to this way of looking at the matter, we have that the constant α is analogous to the reciprocal of the coefficient of viscosity, while ϵ finds its analogy in the reciprocal of Young's modulus.

Hopkinson did not, however, find evidence of such a simple law as the above. We find the following statement in his Scientific Papers, page 2 (Phil. Trans. 166, II, p. 490, 1876):

> The jar was slightly charged and insulated, and the potentials read off from time to time. It was found (1) that even after 24 hours the percentage of loss per hour continued to increase, (2) that the potential could not be expressed as a function of the time by two exponential terms. But the latter fact was more clearly shown by the rate of development of the residual charge after different periods of discharge, which put it beyond doubt that if the potential is properly expressed by a series of exponential terms at all, several such terms will be required.

Later, when developing his theory of elastic after effect, he says: "It should be noted that the view of this subject adopted by the author in a previous paper can be included in equation (2), (here equation (40)), by assuming that $f(\omega)$ is the sum of a series of exponentials."

We see, therefore, that if the most obvious assumptions be made in Hopkinson's theory with regard to the law of decay of the elastic after effects, we are led mathematically to Pellat's theory and von Schweidler's modification of the same.

III. SUMMARY AND CONCLUSION

The principal results of this investigation may be summarized as follows:

1. The capacities and phase differences of 13 commercial paper condensers by different English, French, German, and American makers were measured at temperatures ranging from 10° to 35°, and at frequencies lying between 33 and 1000 cycles per second, using bridge methods previously developed at the Bureau of Standards and only briefly touched upon here.

2. The results of these measurements are presented in 26 curves, which show, for each of the condensers studied, the change of capacity and phase difference with change of temperature, and the variation of the capacity and phase difference with change of frequency, the corresponding curves of a representative mica condenser being appended for sake of comparison. These curves show that the changes of capacity and phase difference with changes of temperature and frequency are much larger than the

corresponding changes with mica condensers. In general, these effects of temperature and frequency are larger the larger the absolute value of the phase difference. They are, however, subject to no simple laws. (For the more detailed discussion of the results of the curves, see p. 514 et seq.). Paper condensers are not suitable to serve as standards of capacity, and should not be employed in *alternating-current* work, where it is desired that the capacity shall remain constant, except when a careful study of the condenser, under different conditions of temperature and frequency, has shown that a satisfactory constancy may be expected. The use of paper condensers for *direct-current* measurements is to be condemned.

3. The phase differences observed lie between 6 minutes and the enormous value of 22°. A phase difference of several degrees is not uncommon in commercial telephone condensers. It is shown that the internal resistance of the plates and leads of a paper condenser are often large, especially in the case of telephone condensers made by rolling up together sheets of tin foil and paper. In one example the energy loss in the condenser, external to the dielectric, is at 1000 cycles three times as great as the energy loss in the dielectric.

4. The observed curves are discussed in the light of the following theories of absorption: Maxwell's theory of a heterogeneous dielectric, Houllevigue's theory of a viscous frictional loss of energy, Pellat's theory, and von Schweidler's modification of it, and Hopkinson's theory of elastic after effects. In each case the expressions for the capacity and phase difference are derived, assuming the wave of emf to be sinusoidal.

5. It is shown that Hopkinson's theory, subject to the assumptions made by its author, is mathematically equivalent to von Schweidler's modified Pellat theory.

6. Of all the theories examined that of von Schweidler only could be made to give quantative results in agreement with the observations. In this theory the difference in phase between the current in an actual condenser and that which would flow if the dielectric were free from absorption is assumed to be due to the presence in the dielectric of molecules whose vibrations are

aperiodically damped. To account for the complicated observed relations connecting the capacity and phase difference with the temperature and frequency it is only necessary to assume a different law of distribution of these molecules as a function of the time constant, for each condenser and for the same condenser at different temperatures. It is shown that the observed results may be represented with a good degree of accuracy on the simple assumption that the actual distribution of the aperiodic molecules is equivalent to one in which molecules of only three different values of time constant are present. The constants of a number of the observed curves have been calculated on this assumption, the method of their calculation being indicated. Such results give a clear idea of the reasons for apparent anomalies in some of the curves in the light of this theory. Perhaps the most important application of such calculations is to the determination of the value of the geometric capacity (the ideal value as unaffected by absorption). This method gives a valuable check on the method of extrapolation described by Curtis (loc. cit., p. 482).

In conclusion it may be stated that further progress in the unraveling of the obscure points remaining for solution in the theory of an imperfect dielectric will probably best be attacked in the future by making accurate measurements of the nature of those in this investigation on condensers constructed under known and carefully controlled conditions. For example, it is important to make measurements on pure, homogeneous substances in the solid or liquid form, to settle the question whether such substances are entirely free from absorption, as has often been maintained.[25] The quantitative effect, on the value of the phase difference, of known added impurities also requires investigation, and such experiments will probably suggest other and equally fruitful points for examination in the light of the dielectric theory.

The author is indebted to Professor Rosa for valuable suggestions in the course of the work, and to Mrs. Grover for assistance in making the observations.

WASHINGTON, February 28, 1911.

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[25] Rowland and Nichols. Phil. Mag. (5), **11**, p. 414; 1881. Muraoka, Wied. Ann., **40**, p. 328; 1890. Maclès, Jour. de Phys., 8, p. 631; 1909.

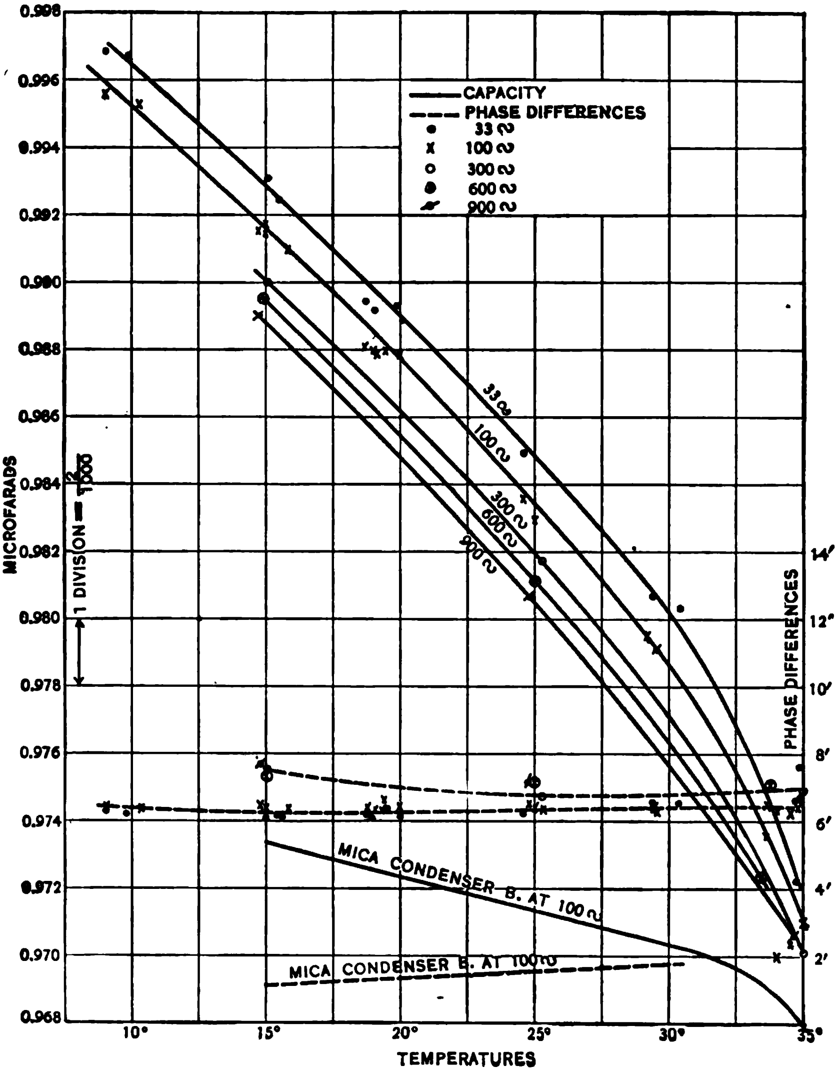

Fig. 5.—*Curves of Capacity and Phase Difference of Mp as Functions of the Temperature*

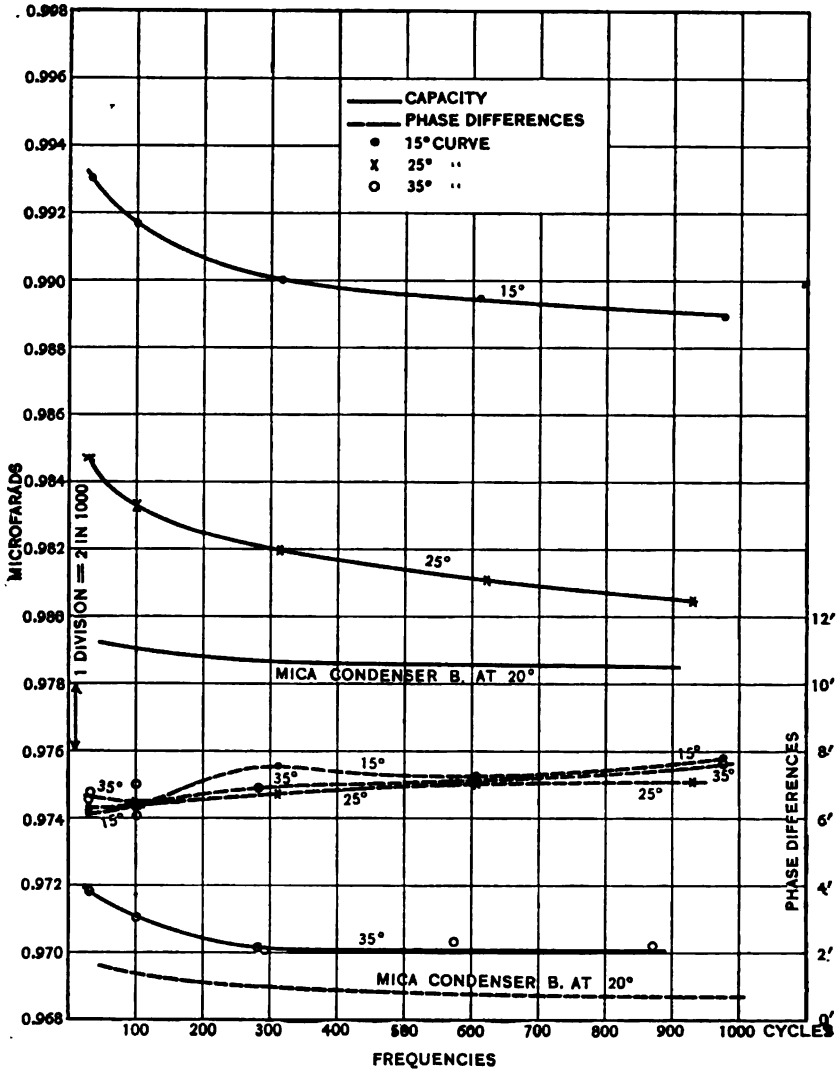

Fig. 6.—*Curves of Capacity and Phase Difference of Mp as Functions of the Frequency*

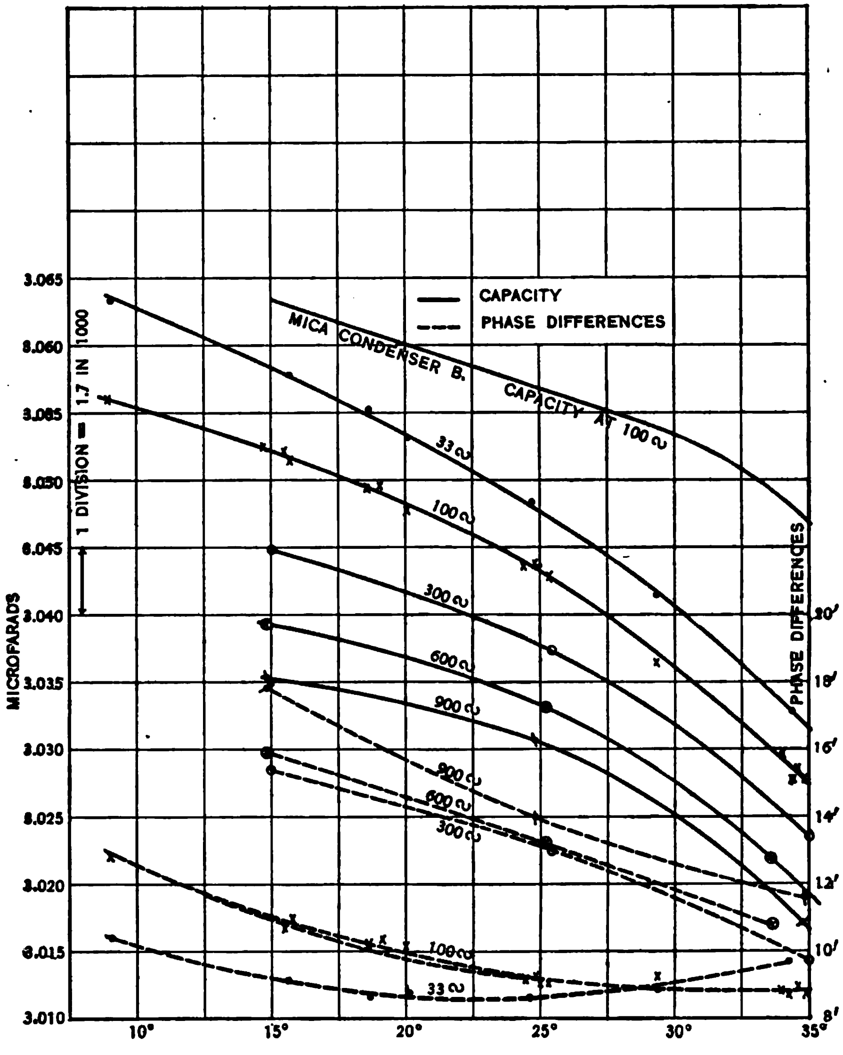

Fig. 7.—*Curves of Capacity and Phase Difference of S_{10} as Functions of the Temperature*

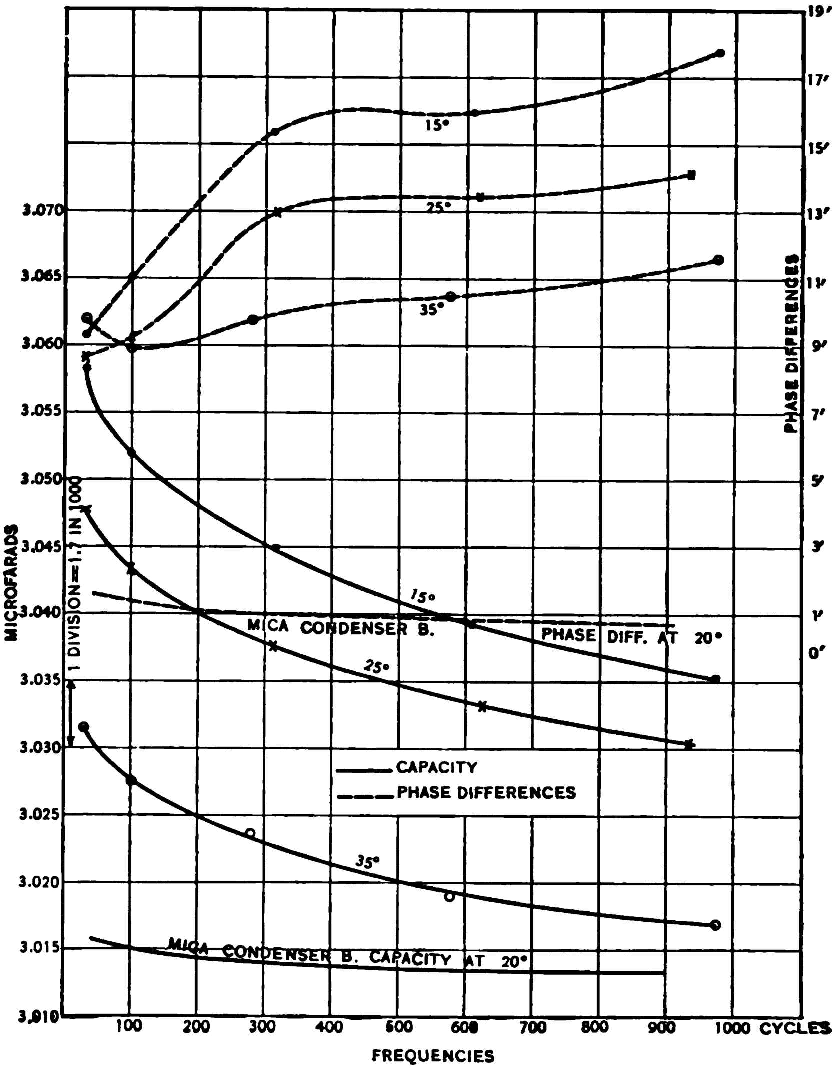

Fig. 8.—*Curves of Capacity and Phase Difference of S_{10} as Functions of the Frequency*

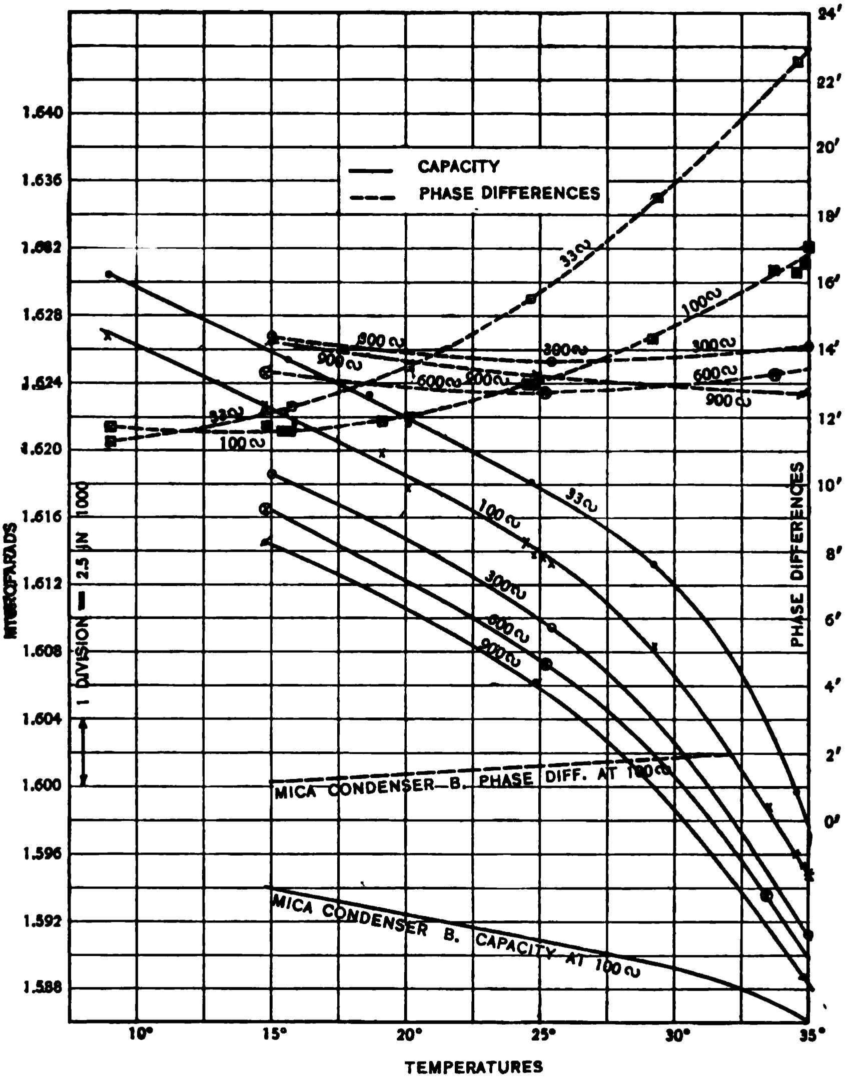

Fig. 9.—*Curves of Capacity and Phase Difference of S_3 as Functions of the Temperature*

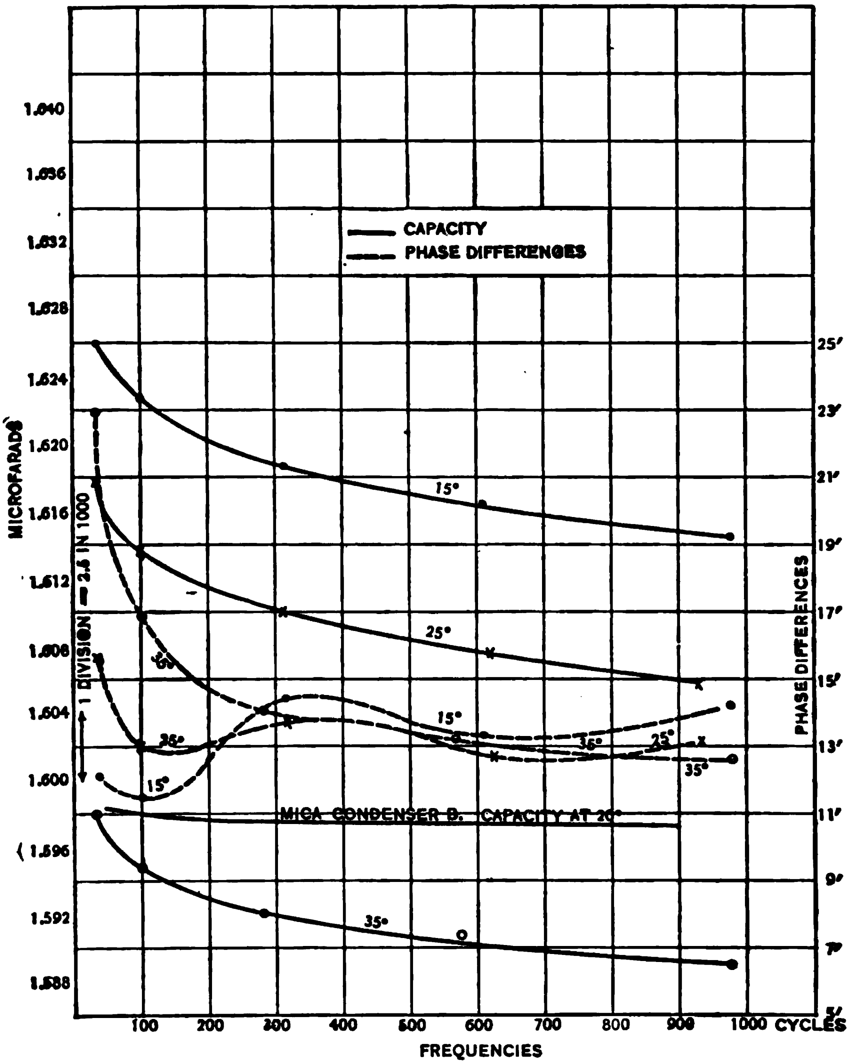

Fig. 10.—*Curves of Capacity and Phase Difference of S_2 as Functions of the Frequency*

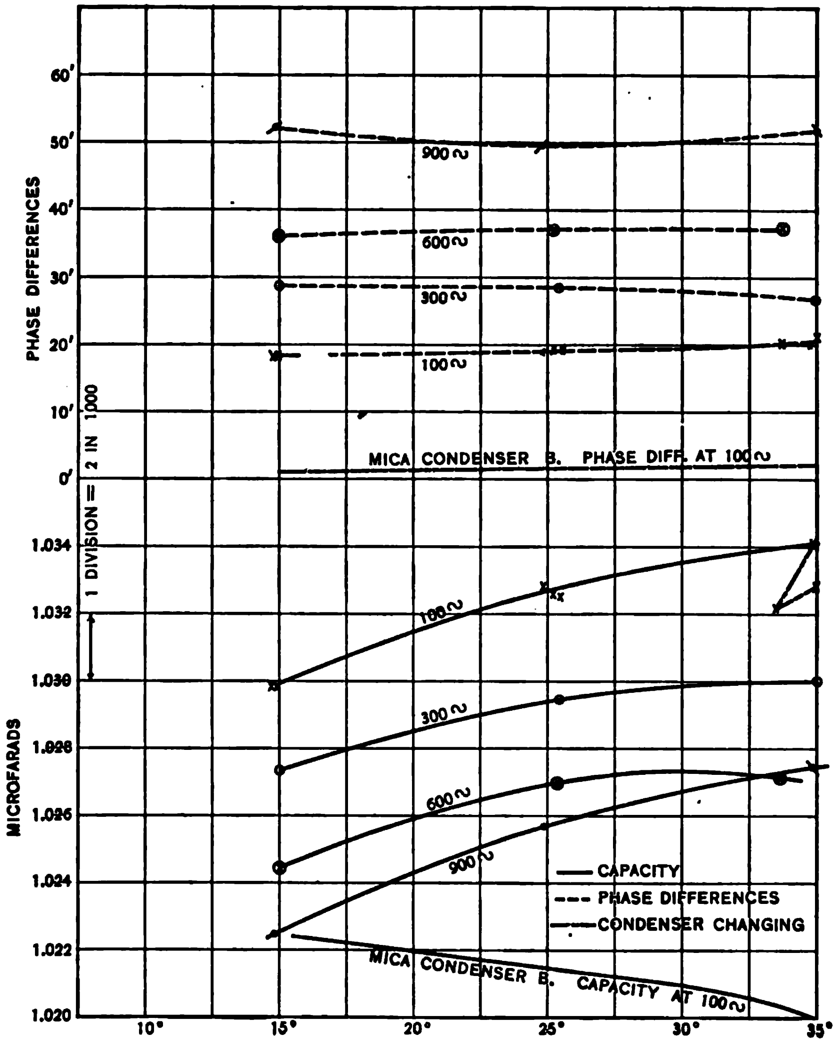

Fig. 11.—*Curves of Capacity and Phase Difference of W_a as Functions of the Temperature*

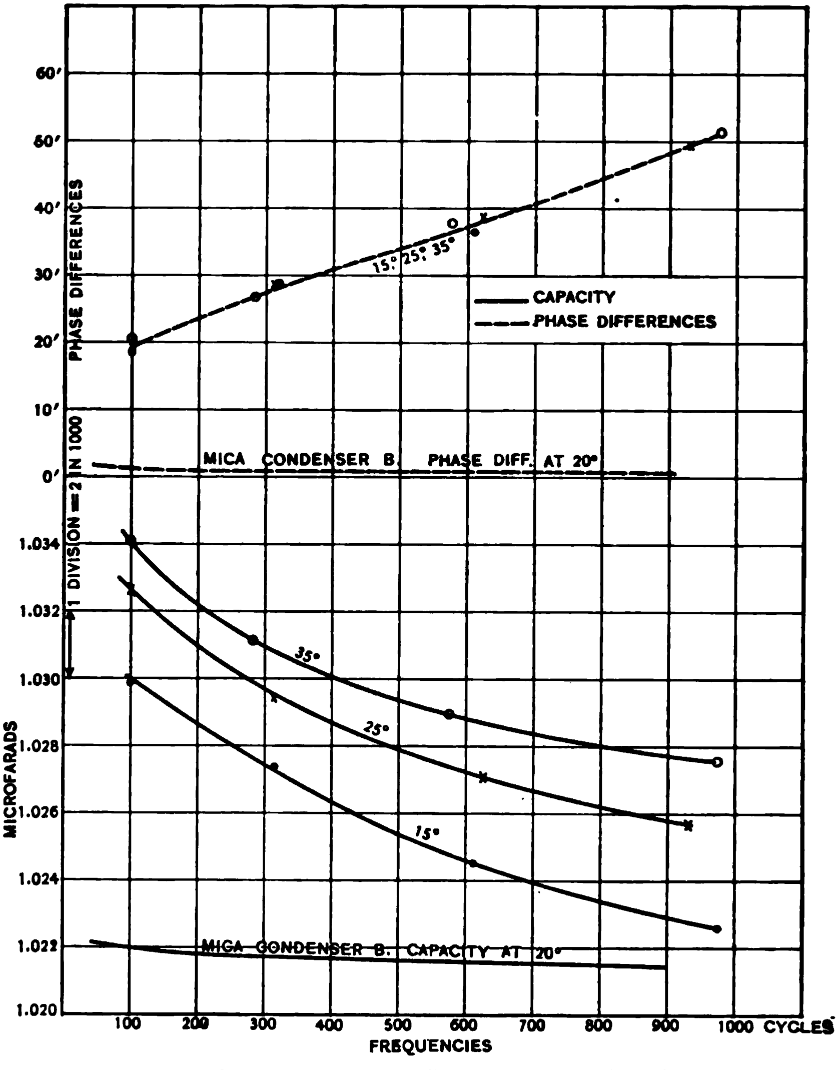

Fig. 12.—*Curves of Capacity and Phase Difference W_a as Functions of the Frequency*

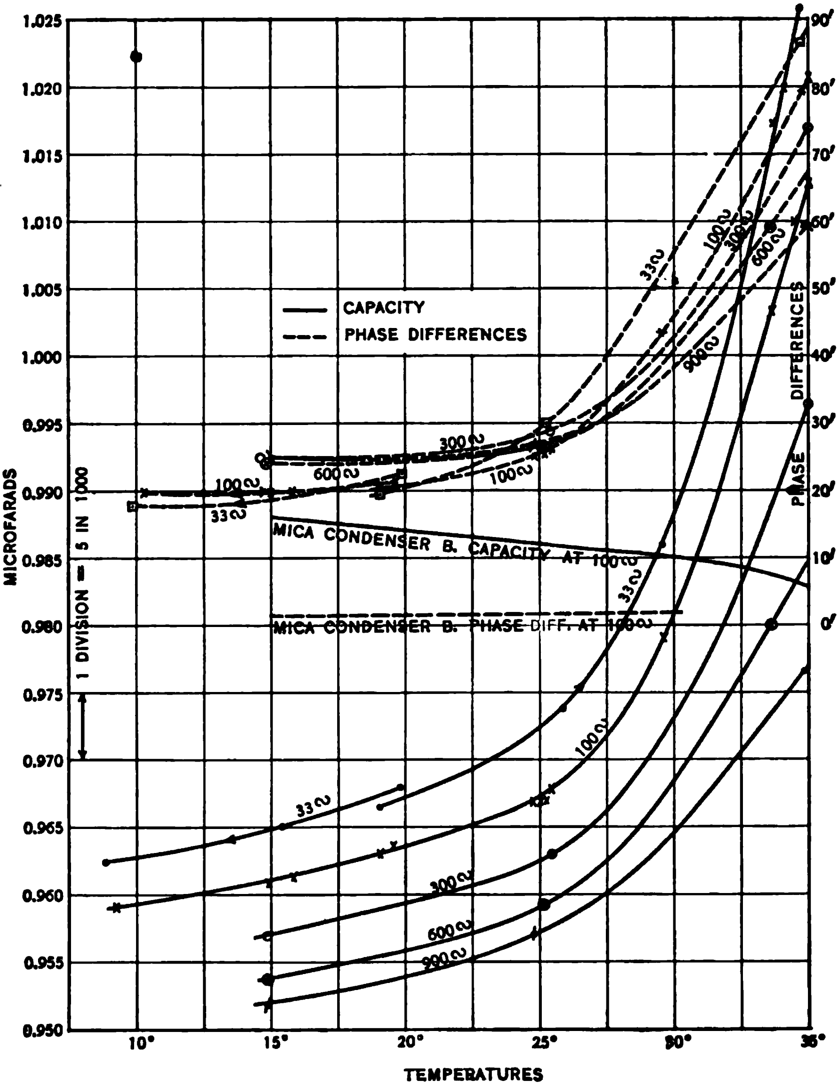

Fig. 13.—*Curves of Capacity and Phase Difference of Lp as Functions of the Temperature*

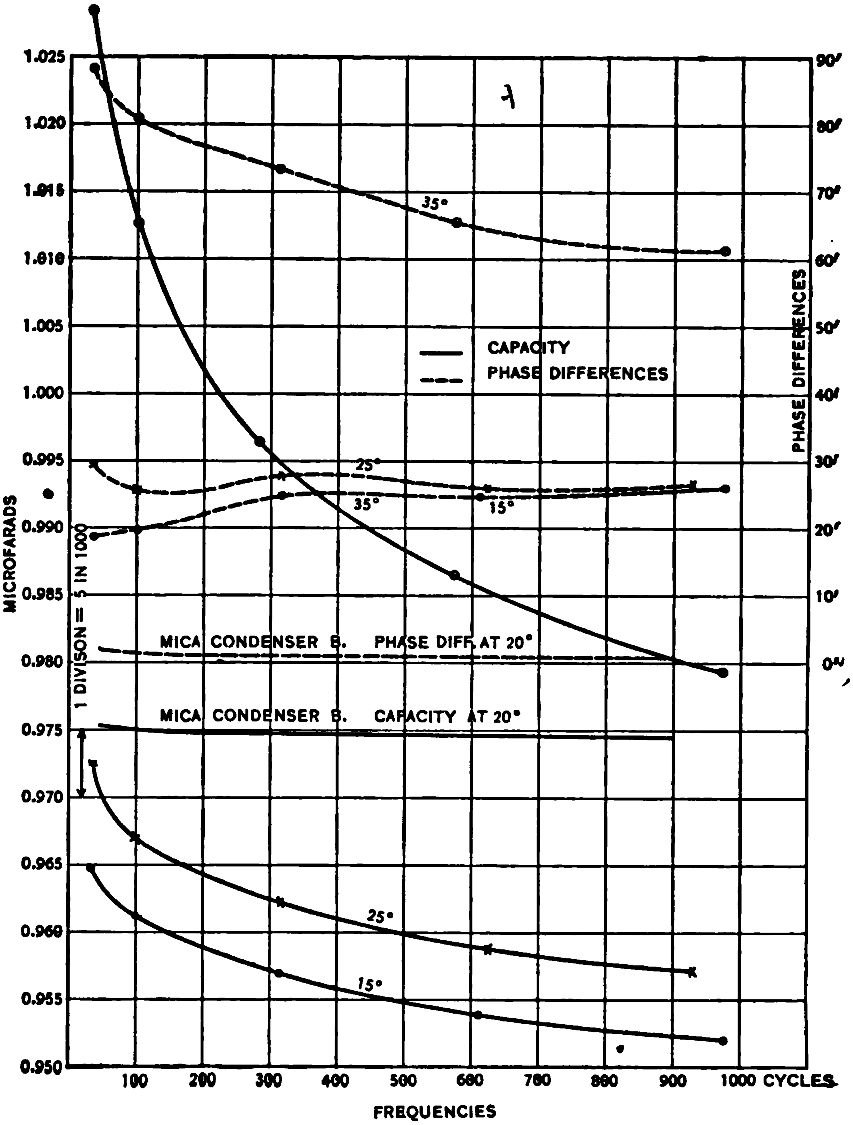

Fig. 14.—*Curves of Capacity and Phase Difference of Lp as Functions of the Frequency*

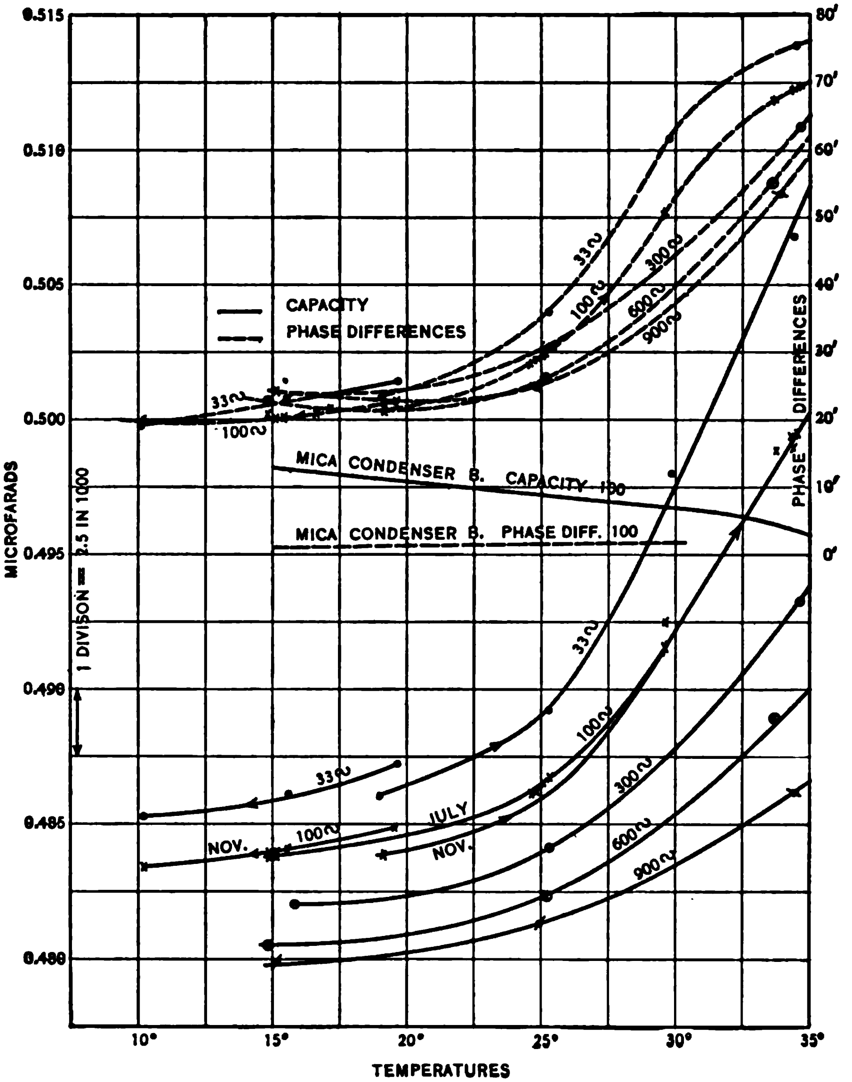

Fig. 15.—*Curves of Capacity and Phase Difference of Cp as Functions of the Temperature*

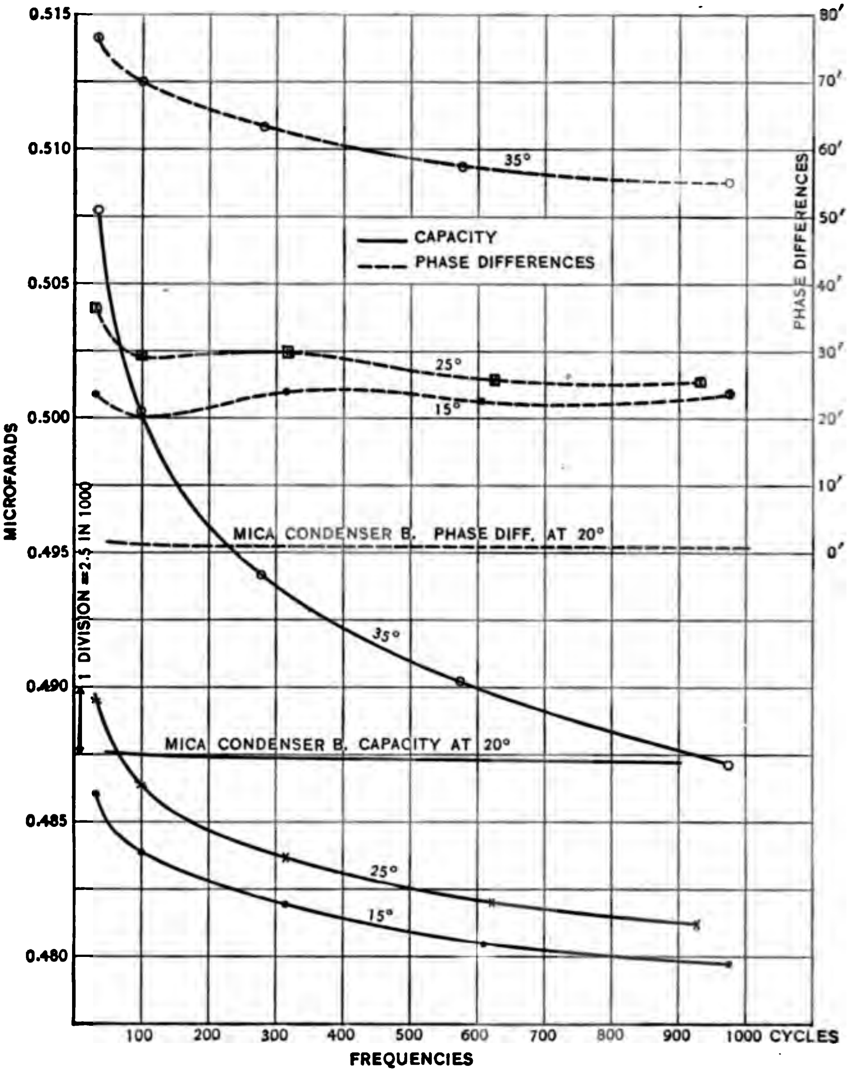

Fig. 16.—*Curves of Capacity and Phase Difference of Cp as Functions of the Frequency*

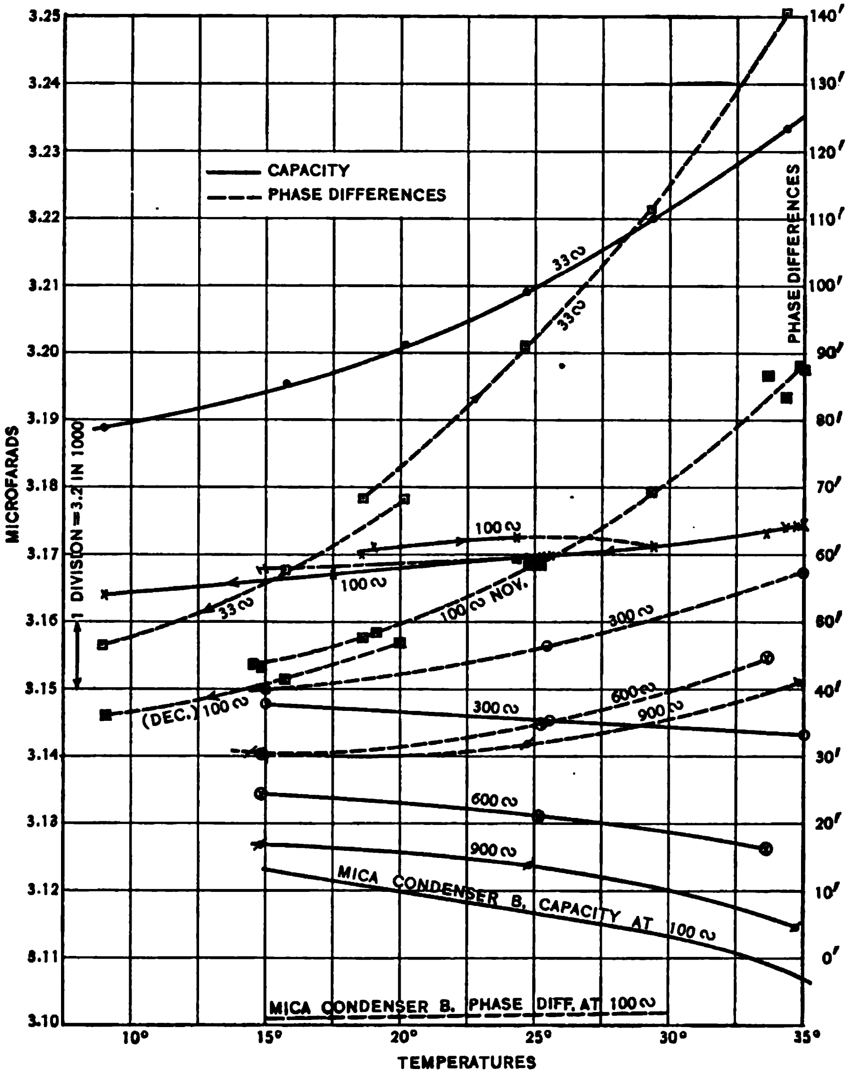

Fig. 17.—*Curves of Capacity and Phase Difference of S_6 as Functions of the Temperature*

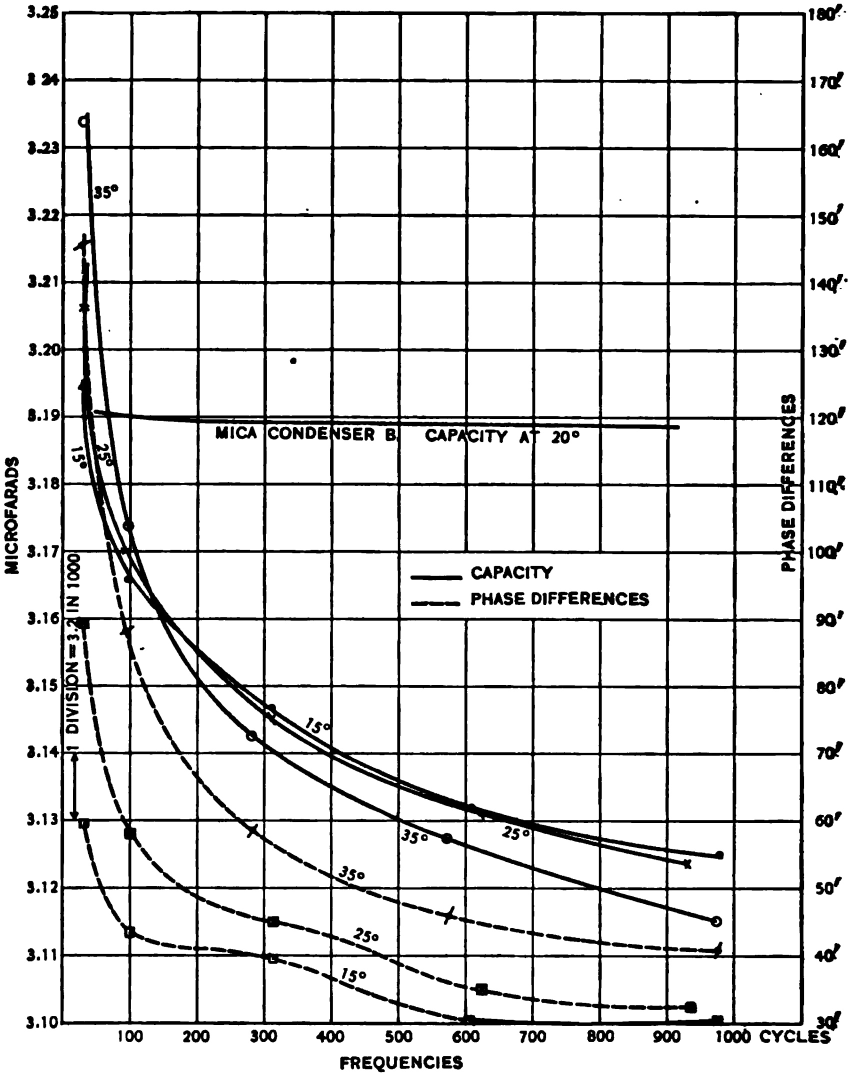

Fig. 18.—*Curves of Capacity and Phase Difference of S_6 as Functions of the Frequency*

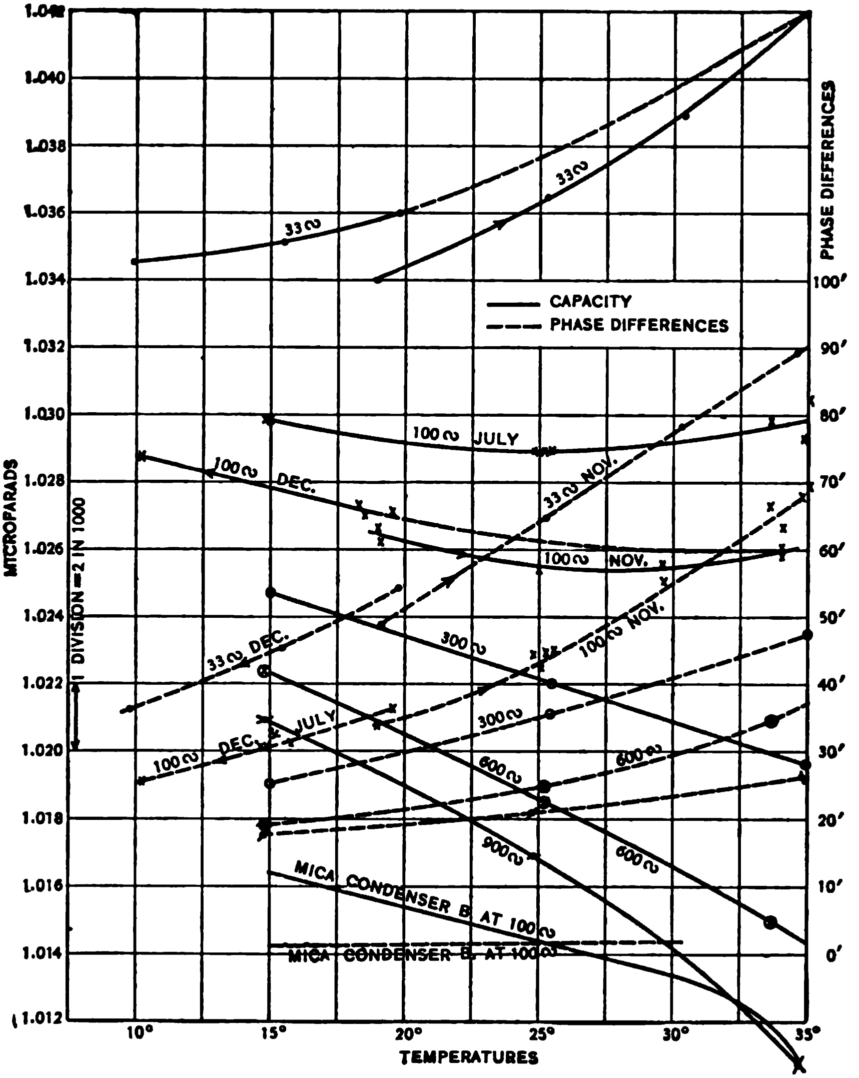

Fig. 19.—*Curves of Capacity and Phase Difference of SH as Functions of the Temperature*

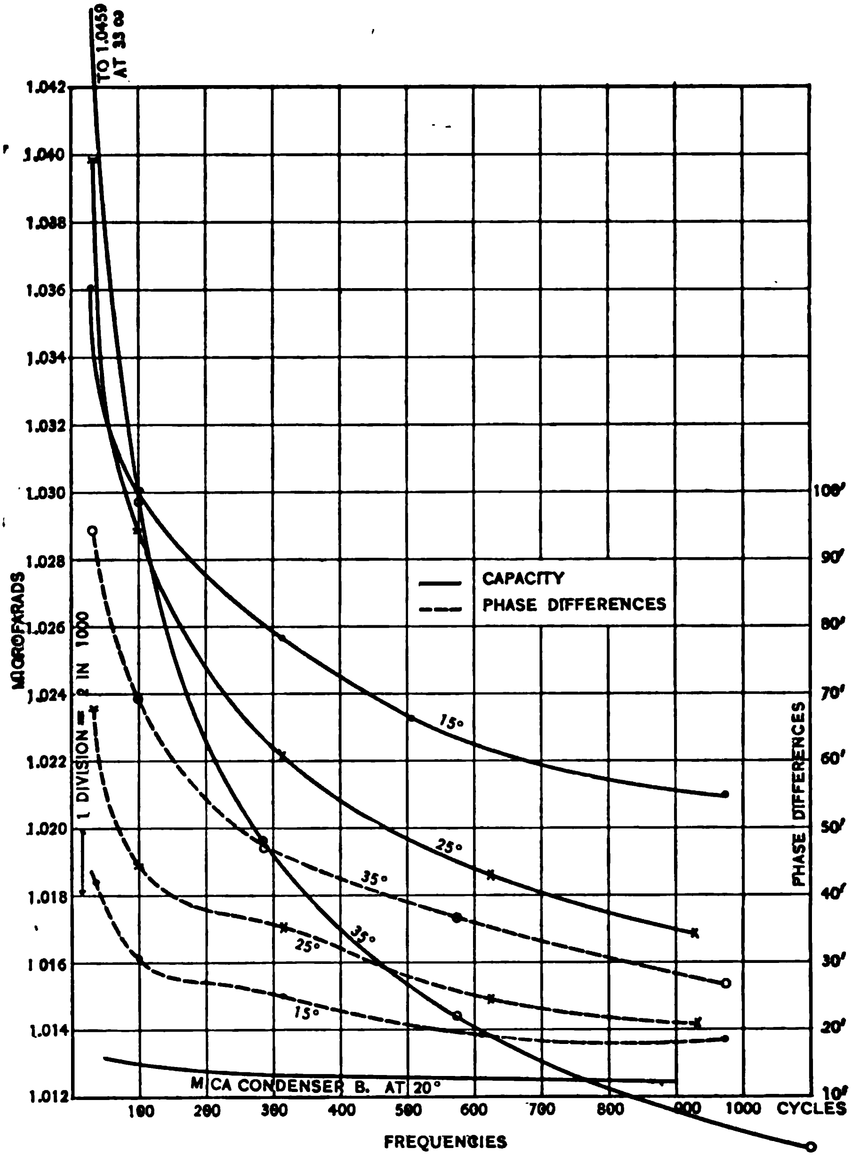

Fig. 20.—*Curves of Capacity and Phase Difference of SH as Functions of the Frequency*

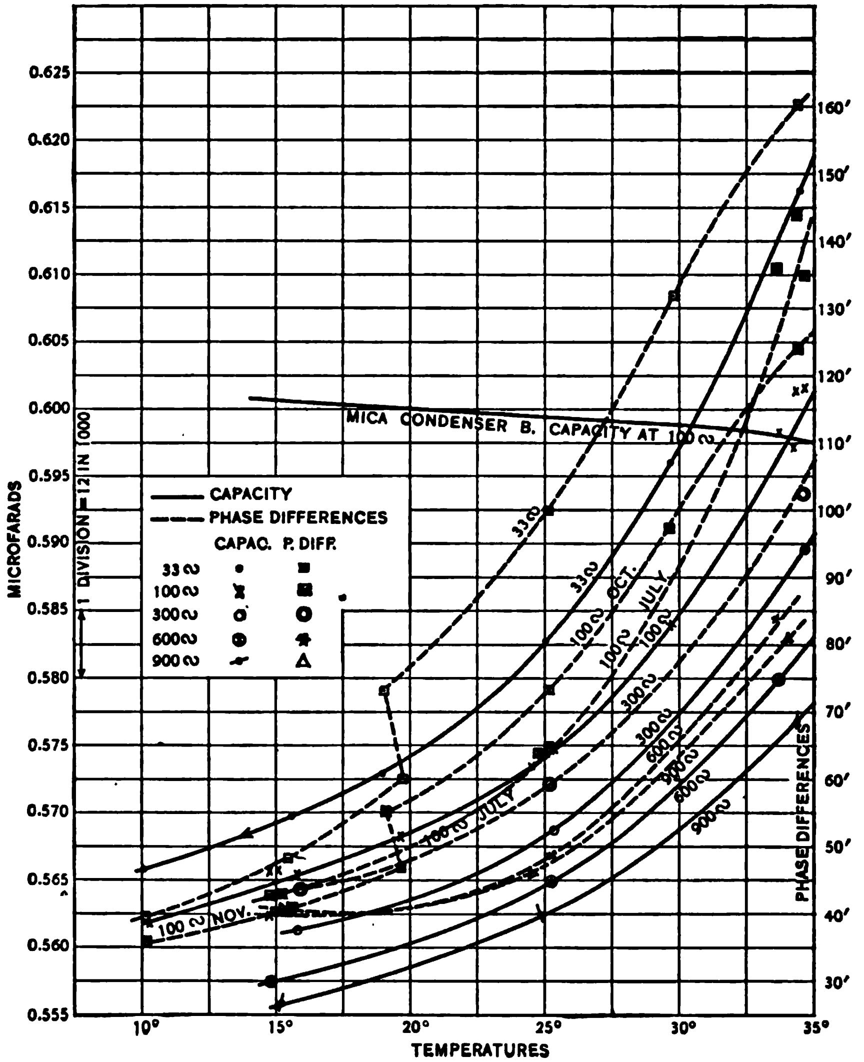

Fig. 21.—*Curves of Capacity and Phase Difference of $Be_{1,8}$ as Functions of the Temperature*

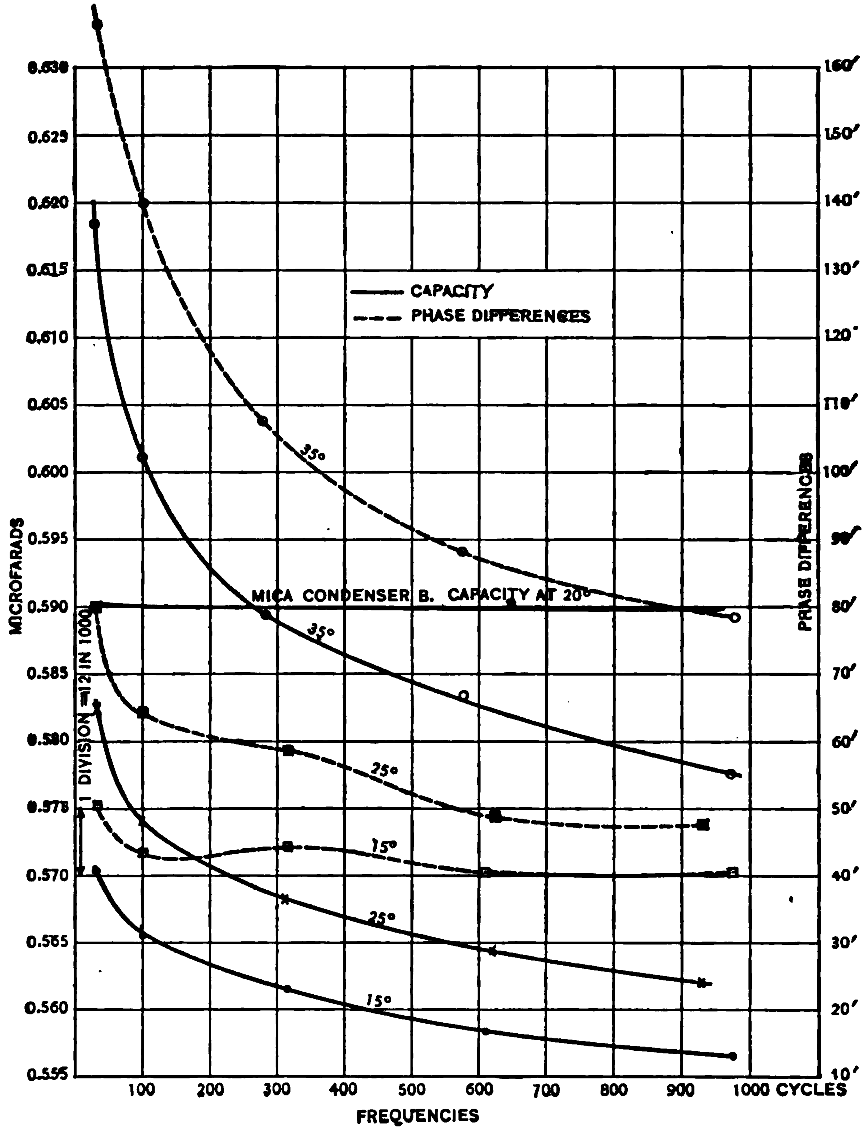

Fig. 22.—*Curves of Capacity and Phase Difference of Be$_{1,5}$ as Functions of the Frequency*

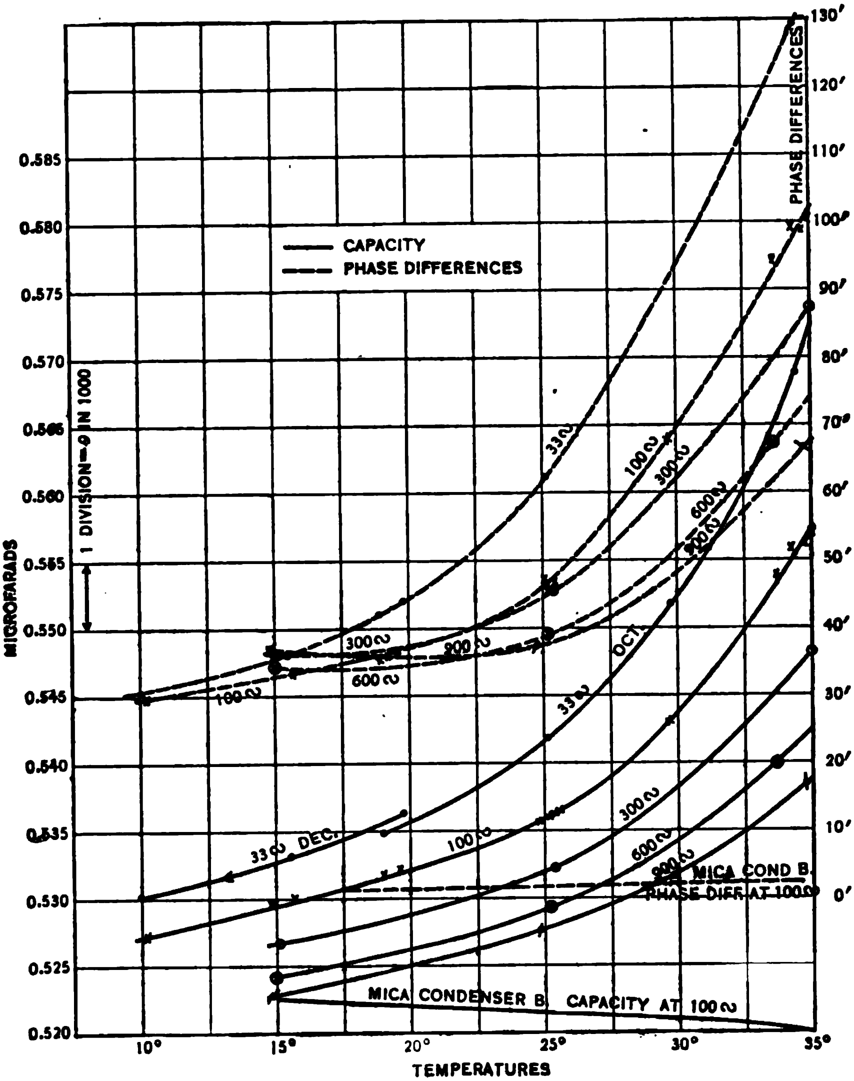

Fig. 23.—*Curves of Capacity and Phase Difference of* $Be_{3,4}$ *as Functions of the Temperature*

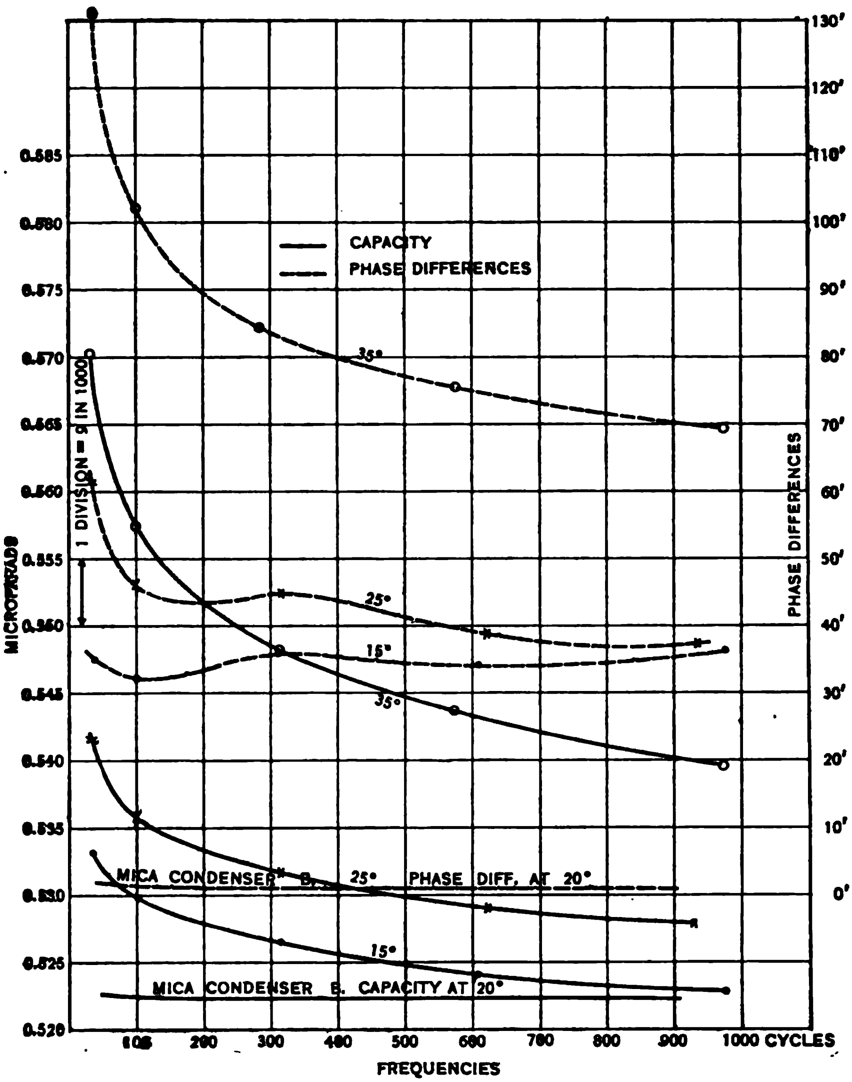

Fig. 24.—*Curves of Capacity and Phase Difference of* $Be_{3,4}$ *as Functions of Frequency*

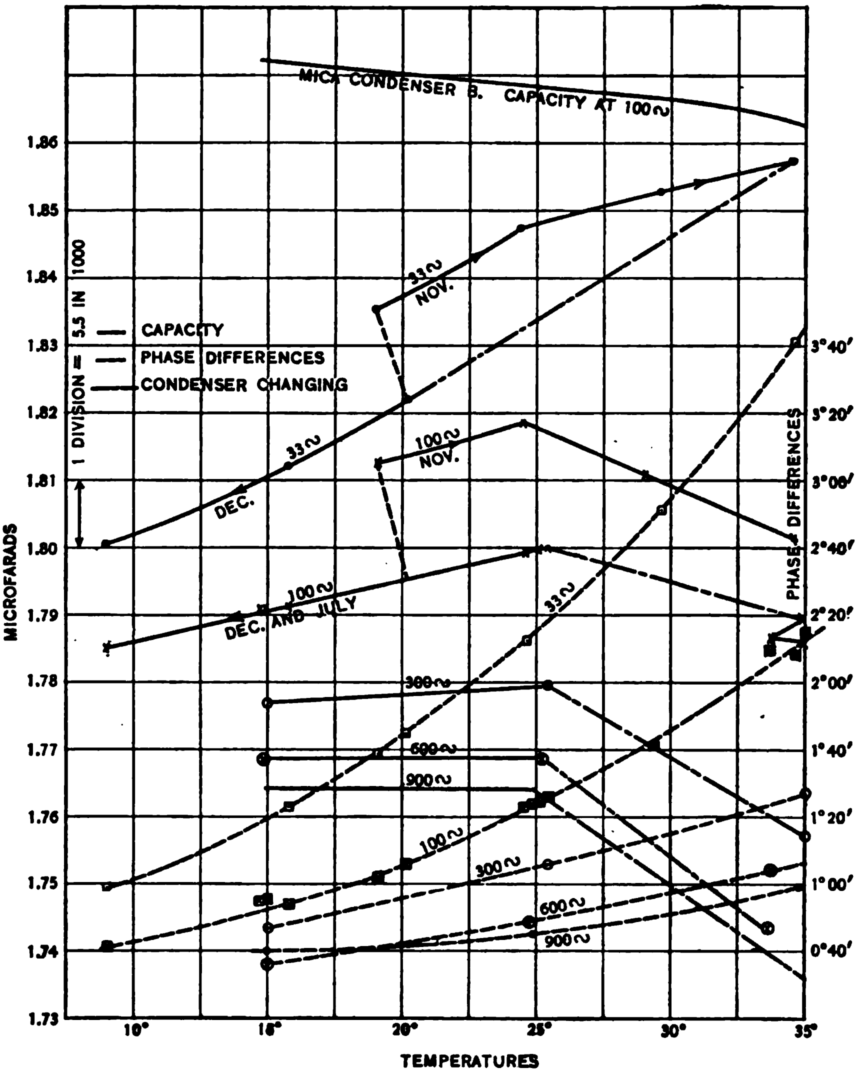

Fig. 25.—*Curves of Capacity and Phase Difference of* T_2 *as Functions of the Temperature*

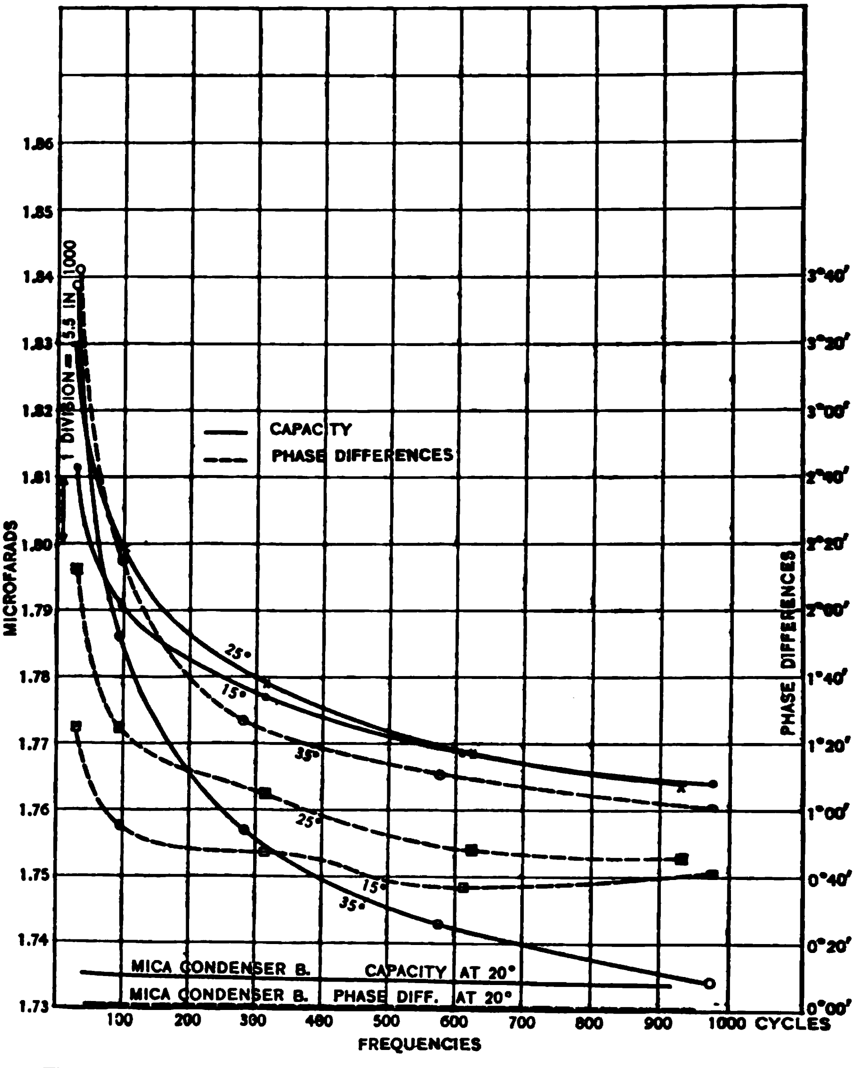

Fig. 26.—*Curves of Capacity and Phase Difference of T_2 as Functions of the Frequency*

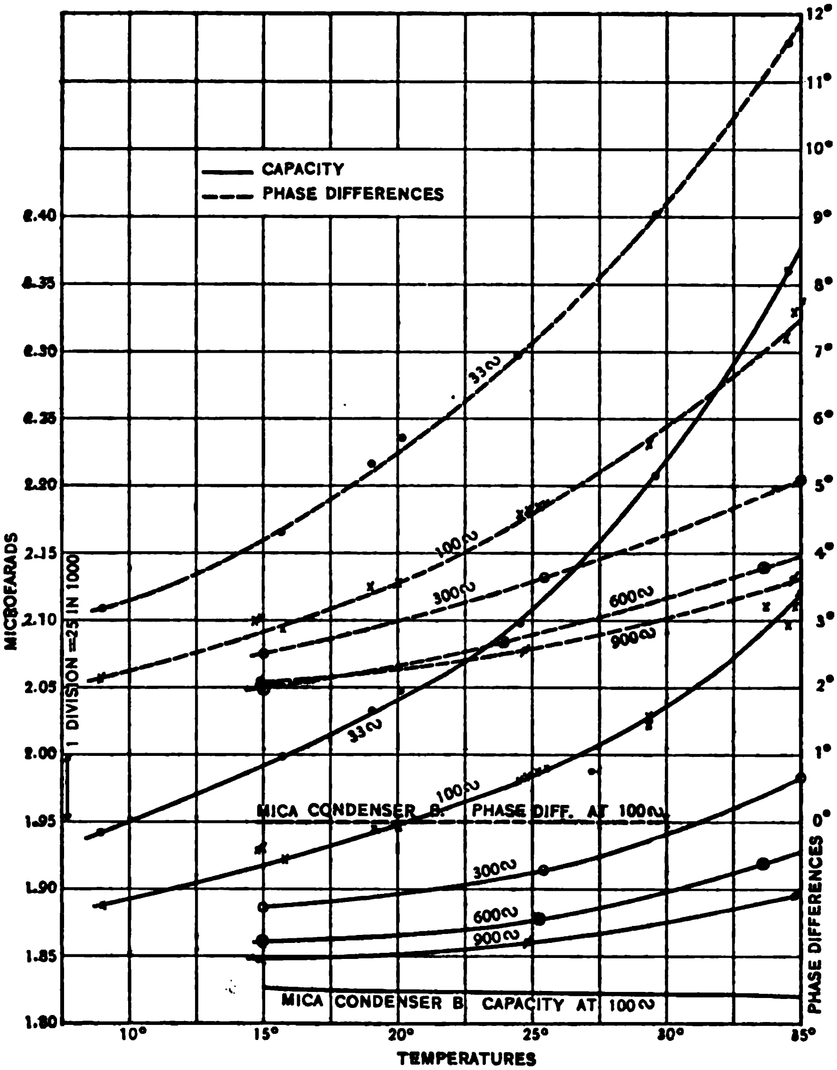

Fig. 27 —*Curves of Capacity and Phase Difference of t_{17} as Functions of the Temperature*

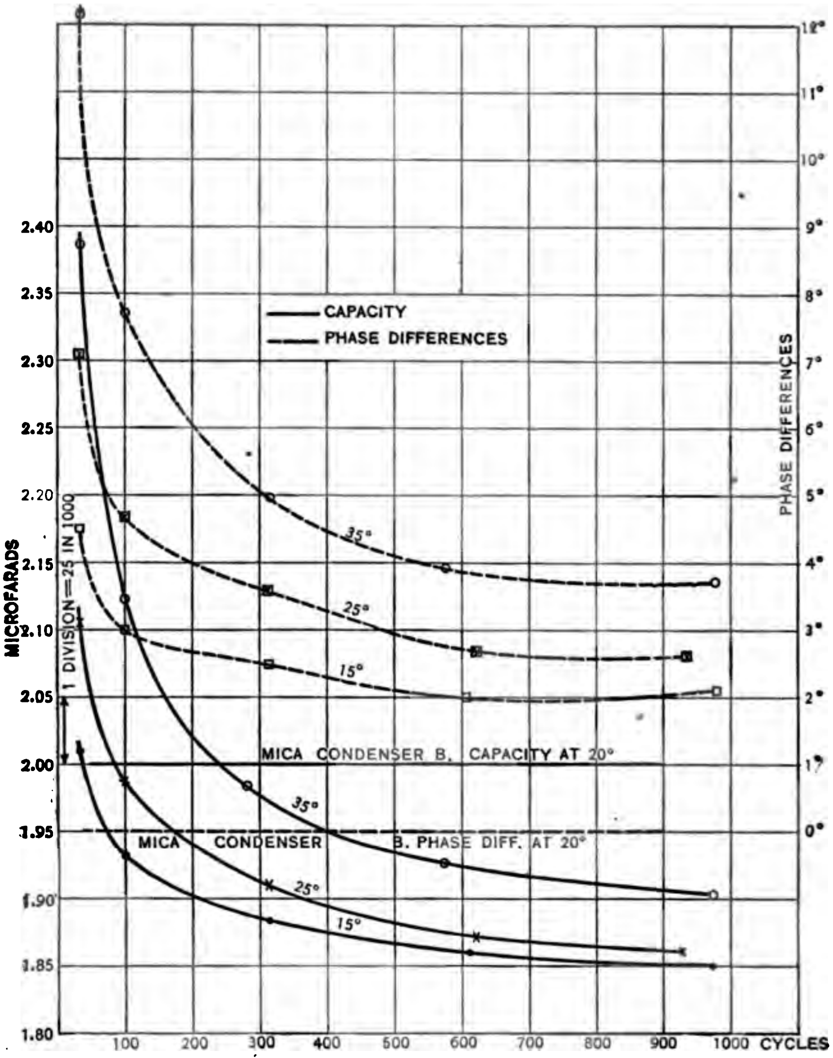

Fig. 28.—*Curves of Capacity and Phase Difference of t_{17} as Functions of the Frequency*

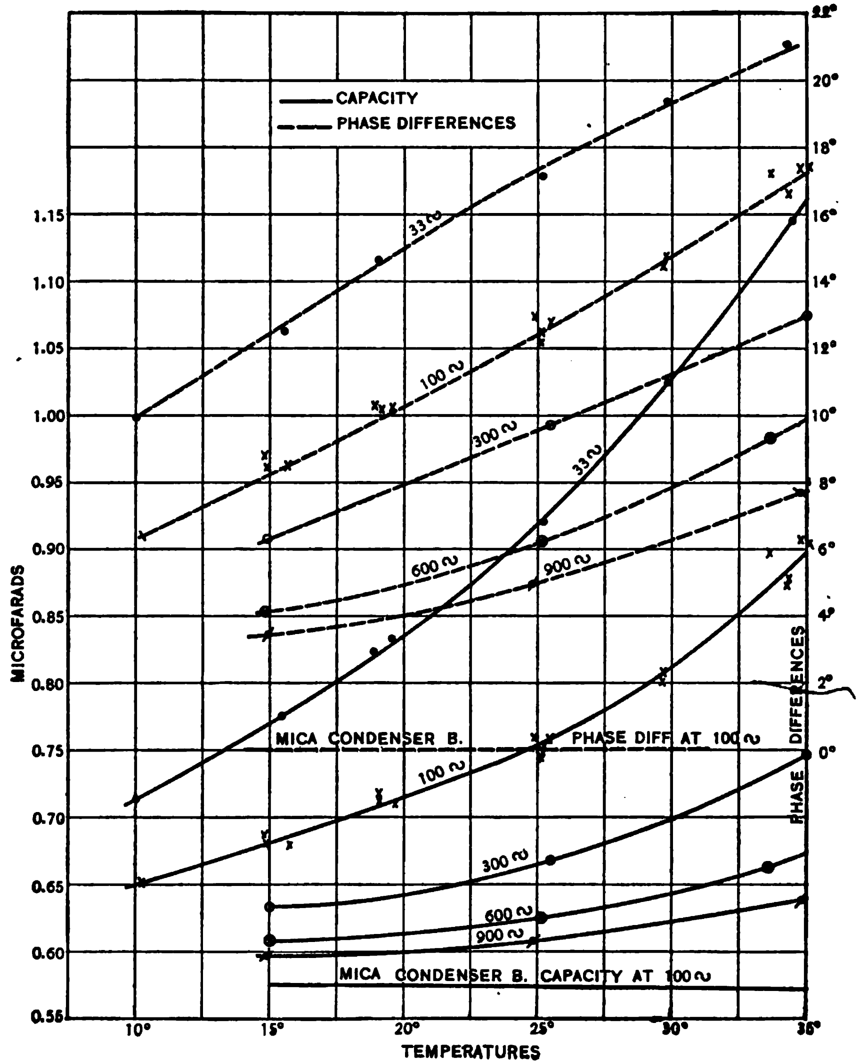

Fig. 29.—*Curves of Capacity and Phase Difference of t_3 as Functions of the Temperature*

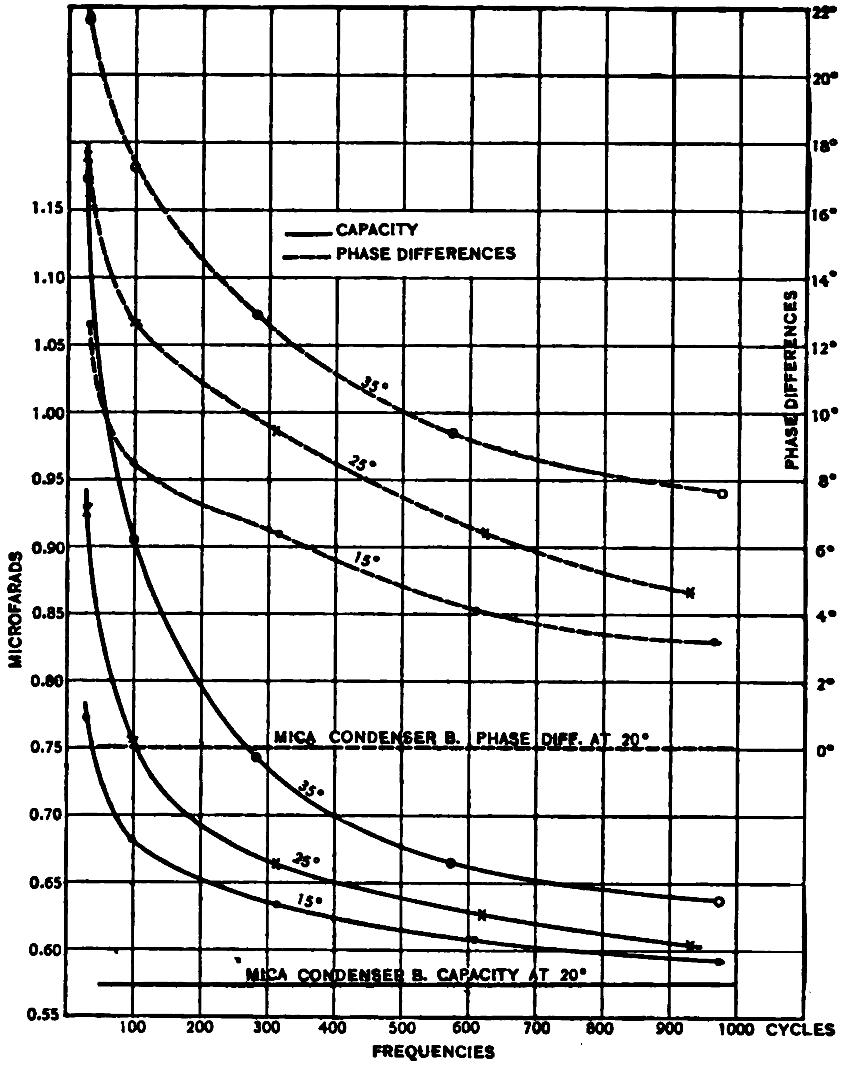

Fig. 30.—*Curves of Capacity and Phase Difference of t_2 as Functions of the Frequency*

THE STEAM-TURBINE EXPANSION LINE ON THE MOLLIER DIAGRAM, AND A SHORT METHOD OF FINDING THE REHEAT FACTOR

By Edgar Buckingham

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INTRODUCTION

The so-called "heat diagram," or $\theta\ \varphi$ diagram, in which the state of a mass of steam is represented by a point on a plane with absolute temperature (θ) and entropy (φ) as rectangular coordinates, has in recent years been much used by writers on technical thermodynamics, and for many purposes it is most instructive, though some caution is needed in interpreting it. But for the quantitative solution of problems in steam-turbine design it is by no means comparable in convenience with the "Mollier diagram" or total heat entropy diagram, in which the representation is on a plane with the total heat (H) and entropy (φ) as rectangular coordinates. The idea of using a surface with H, φ, and p (pressure) as rectangular coordinates is due to Willard Gibbs, H being the same as his "heat function" χ. The H φ diagram may be regarded as the projection of this surface on the H φ plane, and it was introduced to the notice of engineers by Prof. Mollier, of Dresden, by whose name it is commonly known.

The first six sections of the following paper serve as an introduction, for those not familiar with the subject, to some of the technically important properties of quantities H and φ and of the Mollier diagram. The remainder of the paper contains a discussion of the form, on this diagram, of the expansion line for wet steam flowing through a multistage turbine of known stage efficiency, and the development of a practical method for use by designers for drawing the expansion line on the H φ diagram without the use of the laborious step-by-step method.

1. THE TOTAL-ENERGY EQUATION FOR STEADY FLOW OF A FLUID

Let a fluid of any sort be flowing steadily along a channel C_0PC (Fig. 1). Let A_0 and A be two sections of the channel which we shall call the entrance and exit sections.

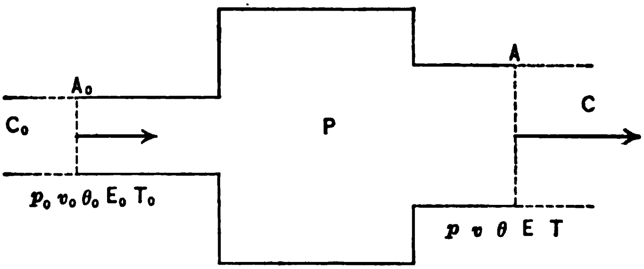

Fig. 1

Let $p_0v_0\theta_0E_0$ be the pressure, specific volume, absolute temperature, and internal energy per unit mass of the fluid as it crosses the entrance section, and let $pv\theta E$ be the corresponding quantities at the exit section. These are to be averages over the section, and the variations from one point to another of the section are to be small.

Let T_0 be the kinetic energy per unit mass at A_0, of the axial component [1] of the velocity, and T the corresponding quantity at A. The channel at A_0 and A shall be varying in cross section so slowly that the kinetic energy of the radial velocity is negligible. If 1 per cent of the total kinetic energy is a negligible quantity, a total taper of one in four, for a cone, is permissible, so that no severe demands are made on the constancy of cross section at A_0 and A.

Subject to the foregoing restriction in the immediate vicinity of A_0 and A, the shape of the channel between A_0 and A is a matter of complete indifference. There may, if we please, be included, as forming a part of the channel or completely inclosed within it, a motor actuated by the flow of the fluid and delivering work outside the channel, or a pump actuated by the application of power from without and doing work on the fluid. The walls of the channel must be tight so as to prevent leakage of fluid, but they need not be thermally insulating. The fluid may be any liquid, vapor, or gas, but for concreteness we shall usually refer to it as steam.

The first law of thermodynamics, if applied to the passage of one pound of steam from A_0 to A, gives us the following statement; the total energy per pound—internal plus kinetic—is increased by the amount of the work done on the steam in crossing the entrance section by the steam behind it, and is decreased by the amount of the work it does against the steam ahead of it in crossing the exit section, by the work given out by the motor, and by any heat which may have been lost by conduction or radiation through the walls of the channel, which may in places coincide with the walls of the motor. We thus have the equation

$$(E+T)-(E_0+T_0)=p_0v_0-pv-W-Q \qquad (1)$$

in which W is the work done outside the channel by the motor, and Q is the heat loss, both measured per pound of steam. The work W includes work done against friction at any bearings which are outside the channel. All the terms in the equation are to be understood as expressed in the same units, e. g., British thermal units (B. t. u.).

---

[1] See note at the end of this paper.

Rearranging equation (1), we have

$$T-T_0+W=(E+pv)_0-(E+pv)-Q \tag{2}$$

which is the first fundamental equation of the theory of fluid motors. It is applicable to regularly acting periodic motors as well as to continuous-flow motors such as turbines, if the quantities in the equation are averaged over an integral number of periods or over any very long time. Since no restriction has been imposed upon the sign of either W or Q, the case of continuously or periodically acting pumps is also included, and the equation is, in fact, valid for all cases of steady or—under the above condition as to averaging—periodically varying flow of any sort of fluid.

2. THE TOTAL HEAT OF STEAM

The quantity $(E+pv)$ has a definite value for every state of the fluid in question and has been designated as "heat of formation at constant pressure," "heat contents," and "total heat." We shall adopt the name total heat and write

$$E+pv=H \tag{3}$$

The quantity to which Regnault gave the name "total heat," and which he measured for dry saturated steam is, for all engineering purposes, sensibly identical with H as just defined. The small outstanding difference is due, first to the fact that the internal energy of water at the ice point is not absolutely though nearly the same at all pressures; and second to the fact that the volume of water at the ice point under any given pressure is not zero though usually quite negligible in comparison with the volume, at the same pressure, of an equal mass of steam dry enough to be suitable for use in a steam motor.

Values of H for water and for dry-saturated steam are given in the steam tables. Their difference is evidently the heat of evaporation, and the value of H for any degree of dryness, x, may be found by linear interpolation between the values for water and for dry steam at the given pressure or temperature. For superheated steam, the value of H is greater than for dry-saturated steam at the same pressure, by the amount of heat needed for the superheating at constant pressure, which depends on the specific heat of superheated steam and is not so well known as might be desired. Convenient tables for saturated and superheated steam are given in the "Steam Tables and Diagrams" of Marks and Davis[3] from which all the steam data used in this paper have been taken.

We may now write equation (2) in the form

$$(T-T_0)+W+Q=H_0-H \qquad (4)$$

The quantity (H_0-H) will, for short, be called the "heat-drop" of the pound of steam during its passage from A_0 to A.

The first two terms of equation (4) represent a quantity of mechanical energy, hence the equation may be read as follows: The mechanical energy produced plus the heat lost to the surroundings, is equal to the heat-drop of the steam. It should be noted that it has not been stipulated that the fluid shall flow without encountering passive resistances such as viscosity. There may be as much internal dissipation of mechanical energy into heat as we please, provided that W represents work actually delivered outside the channel, including work against friction at any *outside* bearings, and that $(T-T_0)$ represents the actual excess of kinetic energy of the axial component of velocity in the exhaust at A over that in the feed at A_0.

3. ADIABATIC FLOW

An adiabatic change of state is defined as one during which the substance in question neither takes in nor gives out heat through its bounding surface. If, therefore, there is no heat leakage through the walls of the channel, the change of state of the steam between A_0 and A is adiabatic. We may then set $Q=o$ and equation (4) reduces to

$$(T-T_0)+W=H_0-H \qquad (5)$$

an equation which has several immediate applications to familiar facts. For example, in the case of steady flow, without heat loss, through a simple tube not containing a motor, the work W is zero and equation (5) says that the increase of kinetic energy is equal to the heat-drop. This is the case of flow through a turbine nozzle or through fixed guide blades, if the flow is so rapid or the channel so well protected that the heat leakage is negligible. In the case of a properly designed, velocity-compounded, impulse turbine, working with a constant pressure within each stage, the velocity and kinetic energy decrease during flow through the intermediate reversing guide blades. Hence T, at exit from these blades, is less than T_0, at entrance to them, and $H>H_0$. The kinetic energy dissipated in the guide-blade channels thus appears in the steam as "reheat" making H larger than H_0.

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[3] Longmans Green and Co. 1909.

The simplest possible case is that of adiabatic throttling or wire-drawing in which there is neither outside work W nor any sensible increase of kinetic energy. The whole first member of equation (5) now vanishes, so that the total heat of the steam remains unchanged during its fall of pressure. Since for steam which remains dry-saturated the value of H decreases with falling pressure, wire-drawing thus tends to superheat dry steam or to dry wet steam, a familiar fact upon which the action of the "throttling calorimeter" is based.

4. DISSIPATIVE FLOW

The passage of heat by conduction or radiation from one point in a body to another involves a waste of availability of the heat thus uselessly let down from a higher to a lower temperature. The internal heating of a body by friction or viscosity involves a waste of the mechanical energy dissipated as work done against the passive resistances of friction or viscosity. In either case, the original state of the body, existing before the waste took place, can not be reestablished except by interference from without; and if we take into account all the bodies involved, the outside bodies used as well as the one concerned in the original process, the initial state of all of them can never be reestablished at all by any means whatever.

Such processes are known, in thermodynamics, as "irreversible" processes. No physical process is entirely free from such elements, and all real changes are therefore irreversible. But if these wasteful elements of the change are relatively so insignificant as to be of negligible importance, the change is sensibly though never exactly "reversible." Evidently any process from which we desire to get as much work as possible should be freed as far as may be from all causes of waste, i. e., of irreversibility.

The wire-drawing of steam through the ports during admission to the cylinder of a reciprocating engine, especially at the cut-off point and at the beginning of admission with incomplete cushioning, is an irreversible and wasteful action to be avoided as far as may be. The expansion between complete cut-off and the opening of the exhaust valve is, *so far as the steam itself is concerned*, sensibly free from internal irreversible actions and therefore internally reversible, in the thermodynamic sense, though on account of the effect of the cylinder walls it is usually far from adiabatic.

The expansion of steam through a turbine nozzle or through blade channels of decreasing section would, in the ideal case, be free from dissipation, i. e., not retarded by frictional or viscous resistances, and would be in the thermodynamic sense reversible if so rapid that no sensible interchange of heat took place between different parts of the steam. In practice, there are always resistances due to skin friction and eddy currents; some mechanical energy that might otherwise be produced is thus dissipated into heat and the process is irreversible. Since these resistances are wasteful, it is evident that the smaller they are and the more nearly reversible the expansion is, the more closely the gain of kinetic energy $(T-T_0)$ approaches the theoretically possible maximum which is determined, if there is no leakage of heat, solely by the initial state of the steam and the final pressure to which expansion takes place in the space into which the steam jet issues.

During the expansion of steam between any two points in its path through a turbine, the whole mechanical energy produced, or $(T-T_0+W)$, also approaches its ideal maximum value as all the internal losses due to skin friction and eddy currents in nozzles or blades, windage, and wire-drawing of steam which leaks past blade tips or through bushings, approach zero. The only difference between this case and that of flow through a nozzle is that in the nozzle or in fixed blades the work is necessarily exactly zero, while in the more general case W may have a finite value and $(T-T_0)$ is often negligibly small in comparison with W.

5. ISENTROPIC CHANGES OF STATE

If, during a reversible isothermal expansion at the absolute temperature θ, a body—e. g. a pound of steam—takes in from without a quantity of heat Q, the quantity $\frac{Q}{\theta}$ is known as the "increase of entropy" of the body. Thus, during the evaporation of one pound of water at constant pressure and temperature, ending in its conversion into a pound of dry-saturated steam, the increase of entropy is equal to the latent heat divided by the absolute temperature. This quantity is given in the steam tables as "entropy of evaporation."

If a reversible change of state occurs during which the temperature of the body is not constant, we may cut the process up into a number of small steps; for each of these divide the heat taken in by the average temperature of the body during that step; and finally add all these small quotients. If we then reduce the length and increase the number of the steps indefinitely, the sum approaches a definite limit expressible in the form $\int_A^B \frac{dQ}{\theta}$ where A and B are the initial and final states. The value of this expression is the same for all reversible changes which lead from the state A to the state B, and it is known as the increase of entropy of the body during the change A B. The elementary case of an isothermal change, considered above, is evidently included in this more general definition of change of entropy.

If, as is usual, we take the temperature of the ice point and the pressure of one atmosphere as our standard conditions, the entropy of a mass of fluid at any other temperature and pressure, referred to this standard state, is the value of $\int \frac{dQ}{\theta}$ from the standard to the actual state along a reversible path; and this value depends only on the end state reached and not on how the body actually reached it, if we assume, as is permissible, that the end state *could* have been reached by a reversible process.

In an adiabatic change of state, dQ is everywhere zero. Hence if an adiabatic process is also reversible, the entropy of the body in question does not change. Any change of state in which the entropy of the body remains constant is known as an isentropic change.

The ideal adopted for the expansion of steam in the cylinder of a reciprocating engine is that of expansion without wire-drawing or other irreversible internal losses, in a perfectly nonconducting cylinder. Such an expansion would be a reversible and adiabatic, and therefore an isentropic change of state. From this it has come about that the term "adiabatic" is very often loosely used in engineering works with the meaning "isentropic." In reality, however, an adiabatic process need not be isentropic and an isentropic process need not be adiabatic. This becomes so evident in studying steam-turbine theory that there is ground for hope that this confusion of terms may eventually be eliminated from our thermodynamic literature.

If, for example, a pound of steam passes from a state A to a state B, the change of its entropy is definite and depends only on A and B. If the actual process is irreversible because of internal dissipation by which heat is produced within the steam, the increase of entropy is *not* to be found by taking the value of $\int_A^B \frac{dQ}{\theta}$ along the actual irreversible path, but is greater than this. For heat generated internally has the same effect in changing the temperature or otherwise influencing the state of the steam as an equal amount of heat added from without, so that the final state reached is not the same as if there had been the actual addition of heat from without but no internal generation of heat.

In any actual expansion between two given completely defined states, the final entropy of the expanding substance is always greater than can be accounted for by taking the value of $\int_A^B \frac{dQ}{\theta}$ with Q representing only heat added from without, for even in the best case there is always some internal dissipation. This excess represents heat produced by dissipation of mechanical energy which might, with ideally perfect arrangements, have been saved and used. It is therefore a measure of the wastefulness of the process of expansion. Irreversibility, wasted availability of energy, dissipation, and needless increase of entropy, are merely different aspects of the same thing. One main reason why entropy, which has been somewhat of a stumbling block in technical thermodynamics, is retained, is that its changes give us the most convenient quantitative expression of the wastefulness or the efficiency of thermodynamic processes from which mechanical work is to be obtained.

The expansion of steam in the cylinder of the reciprocating engine is approximately reversible, so far as the steam itself is concerned; the internal losses due to dissipation inside the steam are small, and poor indicated efficiency is due largely to the fact that the expansion is not adiabatic, the influence of the cylinder walls causing the course of the expansion to be different from that desired. The expansion though nearly reversible is not adiabatic and not isentropic.

The expansion of steam in a turbine may be regarded for most purposes as adiabatic, the external losses of heat from the steam to the casing being small. But the process is subject to a great deal of dissipation by eddy currents, etc., so that though nearly adiabatic it is far from being either reversible or isentropic.

The ideal of the steam turbine is thus the same as that of the reciprocating engine, namely, isentropic expansion. In the one case the ideal is not attained because the changes of state of the steam, though nearly reversible, are far from adiabatic; in the other, because though nearly adiabatic, they are far from reversible.

The assumption that expansion through a steam turbine is adiabatic and fails of being isentropic and ideally efficient only because of internal dissipation losses of various kinds is, of course, only an approximation. For, except possibly in some very unusual cases, there is always some heat lost by conduction and radiation from the turbine, and there is always some longitudinal conduction between the different stages, tending to make separate parts of the expansion not quite adiabatic even though it might be so as a whole. External losses might be reduced or even made negative by jacketing; but while this would improve the efficiency of the turbine, considered by itself, the jacket steam used would probably much more than offset the gain and cause a considerable increase in the total water rate. It is possible that with small turbines not well protected the external heat losses might be as great as the internal dissipation and so just balance the reheat. In such a case the total result would be the same as if the mechanical energy actually wasted inside the turbine had been used up on bearing friction outside, with no internal heating and no conduction and radiation loss. The expansion might thus be isentropic without being, even approximately, either adiabatic or reversible.

We shall, however, treat the turbine problem as one of adiabatic expansion, having therefore an isentropic expansion as its ideal, and shall treat the external heat losses as negligible and consider the flow as subject to equation (5). Such a simplification would not be permissible in precise physical work, but for the purposes of steam-turbine design, the errors thus introduced are probably always less than those due to the uncertainties in the values of some of the quantities that have to be assumed in the computations—notably, velocity losses in nozzles and blade channels and windage resistance, both of which influence the efficiency, of which an estimate must be made in order to design at all.

6. THE H φ OR MOLLIER DIAGRAM

The total energy equation for adiabatic flow

$$(T-T_0)+W=H_0-H \tag{5}$$

gives us information in terms of the total heat H. We have also seen that the ideal expansion is isentropic, since that corresponds to absence of dissipation and therefore to 100 per cent efficiency in the production of mechanical energy. It is therefore evident that for the graphical solution of problems in steam flow—turbine design in particular—a chart showing the properties of steam on a plane with the total heat H and entropy φ as rectangular coordinates will be very convenient. On this plane, if H is made ordinate and φ abscissa, an isentropic expansion is represented by a straight line drawn vertically downward from the point representing the initial state; and the heat-drop during the expansion is represented by the length of this line from the initial to the final position of the state point. In any adiabatic expansion whatever, the difference of ordinate of the initial and final points gives us, at once, the heat drop and therefore, by equation (5), the mechanical energy developed.

We have now to mention some of the geometrical properties of the H φ diagram for steam and may refer to Fig. 2, which gives a qualitative idea of the diagram with the isopiestics, or lines of constant pressure, as well as lines of constant dryness and superheat. An exact plot will not be attempted because it is easily available in the above-mentioned tables of Marks and Davis as well as in other books to which it may be presumed that the reader has access.

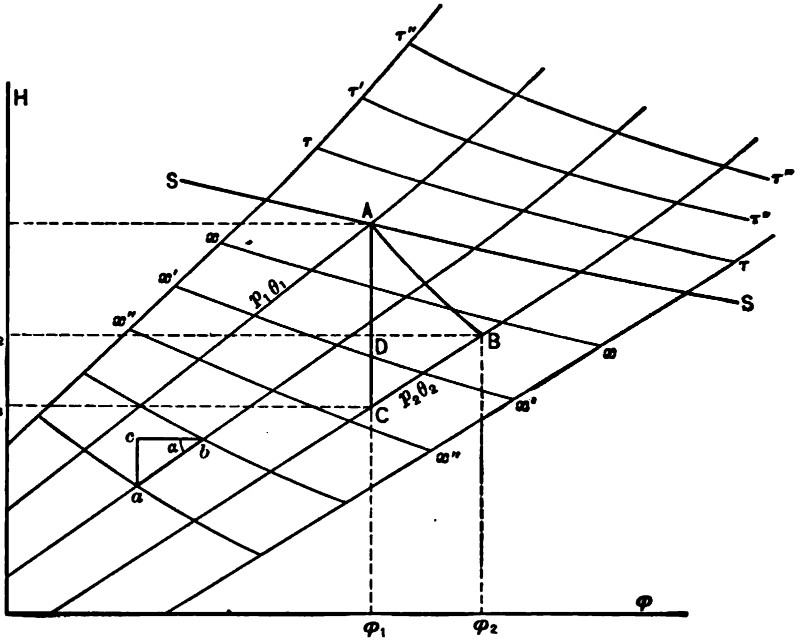


Fig. 2

Vertical lines are isentropics, and horizontal lines are lines of constant total heat or "throttling lines." A vertical distance read off on the scale of ordinates is a difference of total heat or a heat-drop. A horizontal distance represents a difference of entropy.

The steam saturation line *SS* is nearly straight within the range of pressures used in practice. It may easily be plotted by taking simultaneous values of H and φ for dry saturated steam from the steam table. The lines *xx* etc. are lines of constant dryness; points on one of these lines represent the possible simultaneous values of H and φ for wet steam of the given dryness factor x. They run in the same general direction as the saturation line. The lines $\tau\tau$ etc. running also in this same general direction but above instead of below the saturation line *SS*, are lines of constant superheat τ.

The lines we are most interested in are those shown sloping upward toward the right, straight for wet steam, i. e., within the saturation field below *SS*, but curving upward with rising superheat after crossing *SS* and entering the superheat field. These are the constant-pressure lines or isopiestics. Within the saturation field they are also isothermals, since the temperature of wet steam is fixed by its pressure; but above the saturation line they cease to be isothermals, because superheated steam at a given pressure may have any temperature higher than its saturation temperature.

Starting with one pound of wet steam in the condition of pressure and dryness represented by the point a, let us add to it at constant pressure and temperature a quantity of heat represented by the length ac. The state point moves to b, the entropy increasing by an amount represented on the entropy scale by cb. But since the temperature θ is constant we have, by the definition of change of entropy,

$$\text{length of } cb = \text{length of } ac \div \theta$$

these lengths being measured on the scales of H and φ used in drawing the chart. If these scales are the same, $\theta = ac \div cb = \tan \alpha$. If as is usual the scales are different, we have

$$\theta = k \tan \alpha \tag{6}$$

where k is a constant depending on the scales and equal to unity when they are the same.

The slope of the isopiestics for wet steam is therefore proportional to the absolute temperature: the lines have greater slope as the pressure rises and have the familiar fan-shaped arrangement shown in Fig. 2. The reasoning just used is applicable even when the isopiestics are curved, i. e., for superheated steam, if *ac* and *bc* are infinitesimal; so that equation (6) is general if α is understood to be the angle between the φ axis and the tangent to the isopiestic at the given point. There is no sudden change of direction at the saturation line, because there is no discontinuity in the temperature; but with increasing superheat the temperature and therefore, by (6), the slope of the isopiestics increases and they are concave upward, as shown.

Lines of constant dryness drawn for regularly changing values of x, e. g., $x=0.9$, $x=0.8$, $x=0.7$, etc., cut off equal segments on any given isopiestic, and the lengths of the segments on two different isopiestics are proportional to the values of $\frac{l}{\theta}\sqrt{1+\theta^2}$ where l is the latent heat, and $\frac{l}{\theta}$ is the quantity tabulated as "entropy of evaporation."

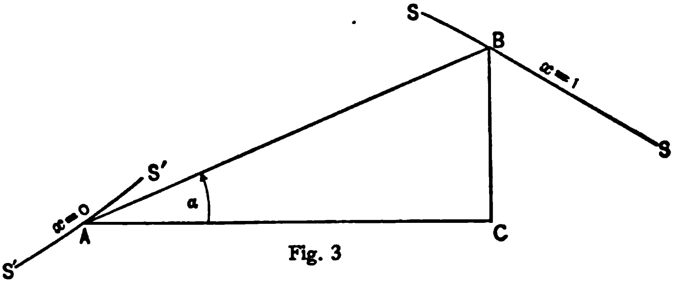


Fig. 3

To prove this we consider Fig. 3, in which *SS* represents the steam saturation line and *S′S′* the water line, i. e., the constant dryness line for $x=0$. The whole length of any isopiestic *AB* between the two saturation lines is given by $\overline{AB}=\sqrt{\overline{AC}^2+\overline{CB}^2}$. But $\overline{CB}=l=$ the heat of evaporation at the given pressure and temperature p θ; while if the scale of φ is the same as that of H, $\overline{AC}=\frac{l}{\theta}=$ the entropy of evaporation. We therefore have

$$\overline{AB}=\sqrt{\frac{l^2}{\theta^2}+l^2}=\frac{l}{\theta}\sqrt{1+\theta^2}$$

If the scales are not the same there will be a proportionality factor different from unity.

Any line of constant superheat crosses all the isopiestics at points where their slopes are greater by a constant amount than their slopes at and below the saturation line.

7. REPRESENTATION OF EXPANSION ON THE H φ PLANE—EFFICIENCY

Let us start with one pound of steam at the pressure p_1. If the steam is dry-saturated, its initial state is represented by the point A (Fig. 2), otherwise by the intersection of the same isopiestic with the appropriate dryness or superheat line. Let p_2 be the final pressure to which expansion takes place. Then C represents the final state reached in isentropic expansion, and $\overline{AC}=H_1-H_3$ is the ideal maximum heat-drop available for conversion into mechanical energy during adiabatic expansion. The ideal yield may thus be read off at once from the scale at the side of the chart and the ideal water rate computed for a steam motor in which steam expands adiabatically from the initial state A to the final pressure p_2. It is necessary to say "the state A" and not simply "the pressure p_1"; for it is evident that on account of the non-parallelism of the isopiestics, this isentropic heat-drop is greater for dry or superheated than for wet steam. This is qualitatively in accordance with the observed fact that, with given limiting pressures, a steam engine or a turbine has a lower water rate when the initial superheat is raised.

In the actual expansion of steam through a turbine to the final pressure p_2, there is internal dissipation and the working of the machine is not ideally efficient. By reason of this dissipation, part of the mechanical energy which might have been obtained with a perfect machine is either not produced at all or if produced is again immediately dissipated. The whole of this lost mechanical energy appears as "reheat" in the steam, diminishes the actual heat-drop, and increases the entropy just as much as if it had been heat added to the steam from without. The final state of the steam at p_2 will therefore be represented by some point B, to the right of and higher than C. The greater the dissipation the farther B will be from the ideal final state C.

The ideal heat-drop being $H_1-H_3=\overline{AC}$, the actual heat-drop is $H_1-H_2=\overline{AD}$, and the reheat is $H_2-H_3=\overline{CD}$. The efficiency of the process in converting available heat into mechanical energy is evidently equal to $\overline{AD}/\overline{AC}$. This is not necessarily the same as what would ordinarily be called the efficiency; for, by equation (5), $(H_1 - H_2)$ goes to the production of the kinetic energy $(T - T_0)$ as well as to the production of the outside work W, which is the important result of the process and commonly the only result considered in computing efficiency. But in general the quantity $(T - T_0)$ is negligible in comparison with the useful work W delivered by the steam to the rotor inside the glands. If this is true and if A and B (Fig. 2) represent the state of the steam in the steam chest and in the exhaust chamber, the efficiency of the machine in the usual sense is given by $\epsilon = \overline{AD}/\overline{AC}$. If ϵ were given a priori, D and therefore the final steam condition represented by B would thereby be fixed.

In order to discuss the efficiency of the separate parts of a multistage turbine we have first to define the term stage. In a multistage impulse turbine, of the Rateau type for instance, points at the entrances to the various nozzles and at exit from the last compartment to the exhaust are "similarly situated." In a turbine of the Parsons type, points in the clearance spaces at entrance to the fixed blades, together with a point at exit from the last moving row to the exhaust space, are "similarly situated." We shall define a stage as the part of the turbine between any two such *adjacent* similarly situated points. This agrees with the usual definition of a stage for the impulse turbine, but not with that sometimes adopted for turbines of the Parsons type in which each row of blades whether fixed or moving is regarded as a separate stage. Our definition makes a "stage" consist of a fixed row and the next following moving row. This use of the term seems more rational than that which divides the turbine into two kinds of stages—the moving rows and the fixed rows—in one of which no work at all is done by the steam on the rotor. At all events, it is convenient for the purposes of this paper and will be adopted.

If, then, we consider not a whole turbine but a single stage, we may say that the change of kinetic energy $(T - T_0)$ through any stage is negligible. In an impulse stage T and T_0 are usually separately negligible; in a Parsons stage the *change* of steam speed is so small as to make $(T - T_0)$ negligible except in the first stage, and since turbines of this type always have a great many stages, an error of this sort regarding a single one is of no importance in regard to the turbine as a whole. If the kinetic energy term is negligible in comparison with W for each separate stage, it is so for the whole turbine, and if ϵ is the efficiency in the usual sense we have (Fig. 2)

$$\epsilon = \frac{\overline{AD}}{\overline{AC}}$$

When ϵ refers to a single stage it is called the "stage efficiency," for, as we shall see in section 9, a distinctive term is needed.

8. FORM OF THE EXPANSION LINE—GRAPHICAL CONSTRUCTION

It is evident that the expansion of steam in passing through a multistage turbine is not a perfectly regular and continuous process

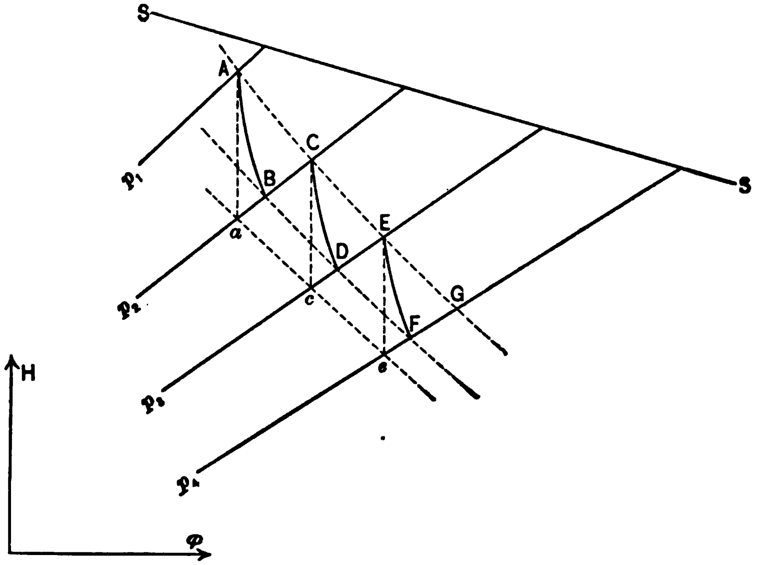


Fig. 4

and that the expansion line can therefore not in reality be a smooth curve like AB in Fig. 2. Let us consider the simple case of a three-stage impulse turbine working with wet steam between the pressures p_1 and p_4, the intermediate pressures at entrance to the second and third stage nozzles being p_2 and p_3.

In the first-stage nozzles the pressure drops from p_1 to p_2 if the machine is properly designed. There is some reheat due to dissipation in the nozzles before the pressure has fallen to p_2, but by far the greater part of the reheat is due to blade losses, windage, leakage, and "carry-over" i. e., the kinetic energy of the steam leaving the last set of moving blades which is in general wasted and not available for driving the issuing steam directly into the next set of nozzles. All these except the nozzle loss occur at the constant pressure p_2. The true expansion through this stage will therefore be represented by a line something like *ABC* (Fig. 4) and for the second and third stages, if of approximately the same design as the first, the true expansion lines will be of somewhat similar shape, as shown at *CDE* and *EFG*. It would evidently be difficult to predict the precise form of the expansion line *ABCDEFG* in all its small details, but fortunately this is not necessary; for in practice we do not need to know the steam condition exactly for every point but only for a few sets of similarly situated points.

Let us suppose, for example, that we want to know the steam condition at entrance to the three sets of nozzles and in the exhaust; this information is given by the positions of the points *A*, *C*, *E*, *G*. Now the position of *C* is fixed if we know the efficiency of the first stage: For if ϵ is this efficiency, we have

$$H_A - H_C = \epsilon_1 (H_A - H_a)$$

in which H_a is the value of *H* that would be reached if the expansion were isentropic and the final state represented by the point *a*. Another similar step from *C* to the next pressure p_3 fixes the point *E*, and a third the point *G*.

The points *C*, *E*, *G* can thus be found if the stage efficiencies ϵ_1, ϵ_2, and ϵ_3 are known. Before designing can begin, they must be known, either by experiment on single stages similar to the ones in question, or by computation from a speed diagram; for the stage efficiency is a datum which is fundamental to the design and can not be dispensed with.

If there were more than three stages the same method might be continued, and for any moderate number of stages this would not be a laborious operation; but the practical problem is not so simple, for in general only the terminal pressures are given while the intermediate pressures are not given but are to be determined in accordance with some further condition. It may, for instance, be desired that the work done on the rotor shall be the same in all the stages. No general solution of the problem can be given in such a case, and a graphical solution by trial and error might with a large number of stages involve a great waste of time which must be avoided if possible.

At this point the problem simplifies itself. Usually we are required to distribute between two limiting pressures a given number of *similar* stages which may be assumed to have the *same stage efficiency* if so designed that there shall be the same heat drop in each. The points A, C, E, G, etc., will then lie on a certain smooth curve of which the form is determined by the constant stage efficiency and the initial state. If this curve can be constructed, we may satisfy the requirement of equal heat drop by distributing the points A, C, E, etc., on this line so as to be at equal vertical distances apart. The points having been thus determined, pressure and quality may be read off from the chart. It will be shown how such a curve may be constructed more easily then by the step-by-step method, if the number of stages is large.

Up to this point we have considered only the similarly situated points A, C, E, G. But let us suppose that what is wanted is not the steam state at entrance to the nozzles but that at exit from them, after the reheat in the nozzles but before the further reheat at the constant lower pressure has occurred. This will evidently be given by the points B, D, F (Fig. 4). If the stages are all alike and the intermediate pressures have been so determined, by distributing A, C, E, G, etc., at equal vertical intervals, that the heat drop is the same in each stage, the steam speed and the reheat will be very nearly the same in each set of nozzles. The reheat after passing the nozzles will then be the same in all the stages and B will be as far below C, measured vertically, as D is below E, F below G, and so on. It is true, this amount can not be determined exactly, but it can be estimated with sufficient accuracy, and furthermore if there are many stages so that the total heat drop in each is itself small, the vertical distance between C and B will be still smaller and no very great error can be made in the position of B. If, therefore, the curve $ACEG$ has been drawn the points BDF, etc., may all be found very easily if any one can be found. The same is true of any other set of similarly situated points.

We have referred particularly to the impulse turbine, but in designing a turbine of the Parsons type a knowledge of the form of the curve through any set of similarly situated points is equally useful. In either case it is essential that we should estimate the steam quality at various points in the turbine, for otherwise the cross-sectional areas can not be properly proportioned to pass the required amount of steam at the velocities for which the blading and nozzles have been designed, the desired pressure distribution will not exist, and the whole working of the machine will depart from the intentions of the designer, presumably to its disadvantage.

Whatever the set of similar points chosen, it is evident that the true expansion line will approach a smooth curve drawn through these points more and more closely as the number of stages between the two limiting pressures increases and the heat-drop through each stage diminishes. We shall speak of this limiting curve, for an infinite number of stages of equal stage efficiencies, as "the expansion line."

9. COMBINED EFFICIENCY OF SIMILAR STAGES IN SERIES—THE REHEAT FACTOR

Let us consider a single stage, of efficiency ϵ, working with either wet or superheated steam between two pressures which differ very little.

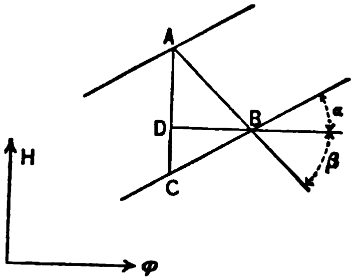


Fig. 5

Let A (Fig. 5) be the initial and B the final state of the steam. To construct the expansion line we may proceed as follows: Measure a short distance AC downward from the initial point. Divide this at D so that $\overline{AD}/\overline{AC}=\epsilon$, the given stage efficiency; then AB will be an element of the expansion line. Go on in the same manner from B, and continue till the lower pressure limit has been reached. The smaller the steps the more approximate the result if the graphical work is exact.

From the geometry of the figure we have

$$\tan\beta=\frac{\epsilon}{1-\epsilon}\tan\alpha \qquad (7)$$

or by equation (6)

$$k\tan\beta=\frac{\epsilon}{1-\epsilon}\theta \qquad (8)$$

As the pressure falls, the temperature θ also falls; hence β decreases and the expansion line is concave upward.

Let us next consider expansion of wet steam through a number of successive stages, of equal stage efficiency ϵ, between the

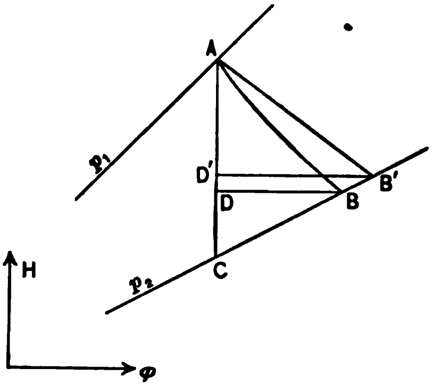


Fig. 6

pressures p_1 and p_2 which differ so that the pressure-ratio p_1/p_2 is a rather large number, 30 for example.

Let A (Fig. 6) be the initial state of the steam and C the state after isentropic expansion to p_2. Let AC be divided at D' so that $\overline{AD'}/\overline{AC}=\epsilon$. Then if the combined efficiency of the whole set of stages were the same as the stage efficiency, the point B' would represent the final state of the steam.

In reality, however, the expansion line starts from A with a sharper slope than the line AB' because the isopiestic p_1 has a sharper slope than the isopiestic p_2. The expansion line then curves gradually, crossing the intermediate isopiestics at such angles that equation (8) shall be satisfied, and meets the final isopiestic p_2 at such an angle that its tangent is parallel to AB' and at a point B which is evidently somewhat below B'. The actual heat-drop AD is therefore greater than AD' and the combined efficiency, $\epsilon_c = \overline{AD}/\overline{AC}$, is greater than the stage efficiency ϵ in the ratio $\overline{AD}/\overline{AD'}$. This ratio is known as the "reheat-factor" and will be denoted by R. Its value, which in practice is seldom greater than 1.1, depends on the ratio of the initial and final temperatures and on the stage efficiency. It could be found in any particular case by step-by-step construction of the expansion line which would give us the position of B, while that of B' is given by $\overline{AD'}/\overline{AC} = \epsilon$. If, on the contrary, the value of R is known, the point B may be found without this graphical work.

We have now to show by a consideration of the form of the expansion line how the value of R may be determined *a priori*, for wet steam, i. e., for any part of the expansion line which lies within the saturation field.

10. FIRST APPROXIMATION FOR THE REHEAT FACTOR R

The total curvature of the expansion line AB (Fig. 6) is fixed by the stage efficiency and the difference in slope of the limiting isopiestics; but the distance BB' and the value of $(R-1)$ depend on how this curvature is distributed, hence on how the isopiestics are distributed between p_1 and p_2. If they change rapidly in direction in the vicinity of p_1, the expansion line AB will curve rapidly at first, B will be close to B' and $(R-1)$ will be small. In the opposite case $(R-1)$ will be large. We have therefore to consider the distribution of the isopiestics.

It will be found, upon examination of an accurate chart, that the isopiestics if produced do not meet in a point; but that their intersections are so far to the left and their whole divergence within the range of pressures used in practice is so small that only a very slight change would be needed to make them all meet in a single point. We shall first proceed upon the assumption that they do thus meet in a single point, comparing the results later with those obtained from a more exact assumption.

Let O (Fig. 7) be the point of intersection of the isopiestics; let H and φ be measured from this point, and let them be plotted

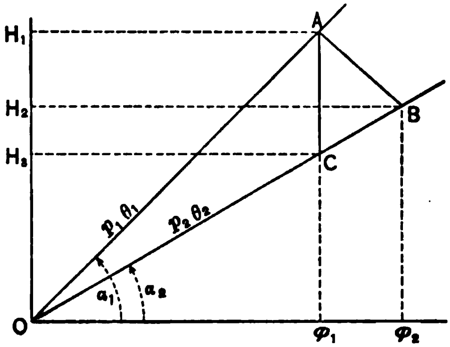


Fig. 7

on equal scales so that $k=1$ in equation (8). We then have to substitute in equation (7)

$$\tan\beta=-\frac{dH}{d\varphi}\quad;\quad \tan\alpha=\frac{H}{\varphi}$$

which gives us

$$\frac{dH}{d\varphi}+\frac{\epsilon}{1-\epsilon}\,\frac{H}{\varphi}=0$$

or, after integrating between any two points on the expansion line,

$$H_2\varphi_2^{\frac{\epsilon}{1-\epsilon}}=H_1\varphi_1^{\frac{\epsilon}{1-\epsilon}} \tag{9}$$

Noting that by the geometry of the figure

$$\frac{\varphi_1}{\varphi_2}=\frac{H_3}{H_2}\quad\text{and}\quad\frac{H_3}{H_1}=\frac{\tan\alpha_2}{\tan\alpha_1}=\frac{\theta_2}{\theta_1}$$

equation (9) may be reduced to the form

$$\frac{H_1}{H_2}=\left(\frac{\theta_1}{\theta_2}\right)^{\epsilon}$$

and the heat-drop from A to B is therefore given by the equation

$$H_1-H_2=H_1\left[1-\left(\frac{\theta_2}{\theta_1}\right)^{\epsilon}\right] \tag{10}$$

If the combined efficiency of the stages were the same as the stage efficiency, the heat-drop would be $\epsilon(H_1 - H_2) = \epsilon H_1\left(1 - \frac{\theta_2}{\theta_1}\right)$ Hence the value of the reheat factor is

$$R = \frac{1 - \left(\frac{\theta_2}{\theta_1}\right)^{\epsilon}}{\epsilon\left(1 - \frac{\theta_2}{\theta_1}\right)} \tag{A}$$

From this equation we obtain, for example, the following values of $(R - 1)$, which give an idea of the order of magnitude:

TABLE I

p_1	p_2	$\epsilon = 0.2$	$\epsilon = 0.6.$
300	50	0.072	0.034
50	2	.096	.047
300	2	.168	.080
300	20	.100	.048
20	1	.083	.040
300	1	.186	.088

11. PRACTICAL WORKING METHOD FOR FINDING THE VALUE OF R

While equation (A) is not very complicated, it is inconvenient because it requires our working with absolute saturation temperatures instead of with pressures, and it would not in this form be of any practical value. We therefore proceed to develop a simpler method for obtaining values of R, which shall be sensibly the same as those given by equation (A).

Values of $(R - 1)$ were computed by equation (A) for expansion from 277.4 pounds to eleven lower pressures, the lowest being 0.31 pound, with stage efficiencies $\epsilon = 0.2$, 0.3....0.7. When these values of $(R - 1)$ were plotted against log θ_2, they gave sensibly a straight line for each value of ϵ. It was found that all the values could be represented very well by the equation

$$R - 1 = 1.207\ (0.975 - \epsilon)\ (log_{10}\ \theta_1 - log_{10}\ \theta_2) \tag{B}$$

If this equation represented equation (A) exactly, we should evidently have the relation

$$(R_{12} - 1) + (R_{23} - 1) = (R_{13} - 1) \tag{C}$$

where R_{12}, R_{23}, and R_{13} are the values of the reheat factor for expansion between θ_1 and θ_2, θ_2 and θ_3, and θ_1 and θ_3, respectively. It will be seen by reference to Table I that this relation is in fact nearly satisfied in the four cases there given.

Taking equation (C) as sufficiently exact, we could then represent equation (B) by a straight line for any given value of ϵ and find the value of $(R-1)$ for expansion with this stage efficiency between any two absolute saturation temperatures, by taking the difference of the ordinates at these two temperatures. If, finally, we plot $(R-1)$ against p as abscissa instead of against the inconvenient $\log \theta$, we shall have reduced our method for finding R to practical shape. A single curve is applicable only to a single value of ϵ, but we may either work to other values of ϵ by means of equation (B), or plot a number of curves for different values of ϵ and interpolate when making the readings of $(R-1)$.

In Table II are values of R computed by equation (B) for expansion from 350 pounds to 18 lower pressures, with the stage efficiencies $\epsilon = 0.1$, 0.2, .. etc. .. 0.8

TABLE II

p_2	$\epsilon = 0.1$	0.2	0.3	0.4	0.5	0.6	0.7	0.8
300	1.0075	1.0066	1.0058	1.0049	1.0041	1.0032	1.0023	1.0015
250	1.0161	1.0143	1.0124	1.0106	1.0088	1.0069	1.0051	1.0032
200	1.0265	1.0235	1.0205	1.0174	1.0144	1.0114	1.0083	1.0053
150	1.0394	1.0349	1.0304	1.0259	1.0214	1.0169	1.0124	1.0079
100	1.0569	1.0504	1.0439	1.0374	1.0309	1.0244	1.0179	1.0114
70	1.0717	1.0635	1.0553	1.0471	1.0389	1.0307	1.0225	1.0143
40	1.0936	1.0829	1.0722	1.0615	1.0508	1.0401	1.0294	1.0187
30	1.1047	1.0927	1.0808	1.0688	1.0568	1.0449	1.0329	1.0209
20	1.1191	1.1055	1.0919	1.0783	1.0646	1.0510	1.0374	1.0238
15	1.1292	1.1144	1.0997	1.0849	1.0702	1.0554	1.0406	1.0258
10	1.1429	1.1265	1.1102	1.0939	1.0775	1.0612	1.0449	1.0285
7	1.1545	1.1369	1.1192	1.1016	1.0839	1.0663	1.0486	1.0309
5	1.1651	1.1462	1.1274	1.1085	1.0896	1.0708	1.0519	1.0330
3	1.1808	1.1601	1.1395	1.1188	1.0981	1.0775	1.0568	1.0361
2	1.1926	1.1706	1.1486	1.1266	1.1045	1.0825	1.0605	1.0385
1.5	1.2102	1.1782	1.1552	1.1322	1.1092	1.0862	1.0632	1.0402
1.0	1.2120	1.1878	1.1636	1.1394	1.1151	1.0909	1.0667	1.0424
0.5	1.2309	1.2045	1.1781	1.1417	1.1253	1.0989	1.0725	1.0460

From these figures any one who desires can plot the set of curves for himself. The curve shown on Plate I was plotted from the values for $\epsilon = 0.1$; for larger values of ϵ the curves would differ from this only in a linear reduction of the ordinates. Having this curve for $\epsilon = 0.1$ we may then find the value of $(R-1)$ by the following practical

RULE: *Read from the curve the values of* $(R-1)$ *at the two pressures between which the expansion takes place; their difference is the desired value of* $(R-1)$ *for* $\epsilon = 0.1$. *For any other value of* ϵ, *multiply by the factor* $\frac{0.975-\epsilon}{0.875}$.

Many numerical tests have shown that values of R found by this rule agree with those found from equation (A) much more closely than any stage efficiency is ever known a priori, the discrepancy being seldom over 0.1 per cent.

The rule may therefore be regarded as a satisfactory substitute for the use of equation (A); but it remains to be shown that equation (A) itself, obtained from an admittedly only approximate assumption regarding the distribution of the isopiestics, gives sufficiently correct values of the reheat factor. This question has now to be taken up.

12. DISTRIBUTION OF THE ISOPIESTICS ALONG AN ISENTROPIC

Let φ_0 be the value of the entropy at some fixed isentropic line. Let Z be used to denote the value of H at a point on this line. In section 10 it was assumed that the isopiestics all met in a single point. If H and φ were both measured from that point we should then have $Z/\varphi_0 = \theta$. If H and φ were measured from some other point, we should have in general

$$\theta = a + bZ \qquad (11)$$

where θ is the absolute saturation temperature of any isopiestic and Z is the value of H at the point where this isopiestic crosses the isentropic $\varphi = \varphi_0$. Equation (11) therefore represents the assumption from which equation (A) was deduced. Readings on the chart show that it is by no means exactly fulfilled. By readings of Z from the $H\varphi$ chart of Marks and Davis at $\varphi_0 = 1.384$, 1.544, and 1.704, it was found that in each case the values could be represented by an expression of the form

$$\log \theta = A + BZ \tag{12}$$

nearly though possibly not quite as closely as the readings could be made. The values of A and B varied with the value of φ_0. A number of readings were made between the isopiestic for $p = 1$ pound and the saturation line. This empirical equation for the change of H during isentropic expansion is one which I do not remember to have seen given and which might prove useful in other work than the present.

Since readings from the chart can not be made with any great accuracy, recourse was now had to interpolation in the tables. Values of H (i. e., of Z) were computed at $\varphi_0 = 1.384$ for 21 pressures from 0.5 pound to 513 pounds. Values of Z for the same temperatures were then computed by the equation

$$Z = 1645 \log_{10}\theta - 3750.2 \tag{13}$$

The greatest difference between Z obtained from the table and Z calculated by equation (13) was 0.7 B. t. u. and the average difference was only 0.3 B. t. u. The differences showed a systematic run, but it was wave-like and not progressive, the value passing through zero in the vicinity of 550°, 700°, and 900° absolute F.

Equation (13) is therefore a quite exact empirical representation of the facts, as given in the tables, over the whole range of pressures used in present steam practice. At any other isentropic where the entropy has the value φ, equation (13) leads evidently to the equation

$$Z = 1645 \log_{10}\theta - 3750.2 + \theta(\varphi - 1.384) \tag{14}$$

which must diverge from the tabulated values by precisely the same amounts as equation (13). For security this was checked through by interpolation in the tables for $\varphi = 1.684$, from the isopiestic $p = 0.505$ lb/in^2 up to the saturation line.

Since equations (13) and (14) are quite exact, it is evident that equation (12), which is equivalent to (13), must be less exact when φ_0 differs much from the value 1.384, though it is an approximation nearly or quite sufficiently close for use with the chart alone.

13. SECOND APPROXIMATION FOR R

Since equation (14) or its special case (13) is a much closer representation of the facts then equation (11) from which (A) was deduced, it follows that an expression deduced from (13) or (14) will give more nearly correct values of the reheat factor than are given by equation (A). We now proceed to deduce such an expression.

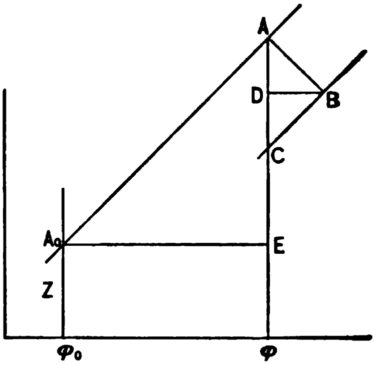


Fig. 8

Let *AB* (Fig. 8) be an infinitesimal element of the expansion line. Then, if ϵ is the stage efficiency, we have

$$\frac{\overline{CD}}{\overline{DA}}=\frac{1-\epsilon}{\epsilon} \tag{15}$$

Now we have

$$\frac{\overline{CD}}{\overline{DB}}=\left(\frac{\partial H}{\varphi}\right)_p=\theta$$

Also

$$\frac{\overline{DA}}{\overline{DB}}=\frac{-dH}{d\varphi}$$

where the symbol *d* refers to change along the expansion line. Substituting these values in (15) gives us

$$\theta\frac{d\varphi}{dH}=-\frac{1-\epsilon}{\epsilon} \tag{16}$$

as an equation which must be satisfied at all points of the expansion line and in all cases, regardless of the distribution of the isopiestics.[3]

---

[3] The validity of this general equation is not limited to the case of wet steam.

Let A_0 be the intersection of the isopiestic through A with the isentropic $\varphi=\varphi_0$, and let Z be the ordinate of this point. Then we have

$$\frac{\overline{EA}}{A_0E}=\frac{\overline{CD}}{DB}=\frac{H-Z}{\varphi-\varphi_0}=\theta$$

Whence

$$\varphi-\varphi_0=\frac{H-Z}{\theta}$$

Differentiating by H and multiplying by θ gives us

$$\theta\frac{d\phi}{dH}=1-\frac{dZ}{dH}-(H-Z)\frac{1}{\theta}\frac{d\theta}{dH} \qquad (17)$$

another general relation, which must hold for all points within the saturation field and for motion of the state point in any direction whatever.

By comparison of equations (16) and (17) we get

$$(H-Z)\frac{d\log\theta}{dH}+\frac{dZ}{dH}-\frac{1}{\epsilon}=0 \qquad (18)$$

If we now let $\phi_0=1.384$, we may, as shown in section 12, set

$$\log\theta=A+BZ \qquad (19)$$

and equation (18) may be reduced to the form

$$\frac{dH}{dZ}=\epsilon\Big[1+B(H-Z)\Big] \qquad (20)$$

a differential equation for the expansion line in terms of H and Z.

This equation is satisfied by setting

$$H=Me^{\epsilon BZ}+Z+\frac{1-\epsilon}{\epsilon B} \qquad (21)$$

in which M is the arbitrary constant, to be adjusted so that the curve shall pass through the given initial position of the state point.

From equation (19) we get $BZ=\log\theta-A$, whence

$$e^{\epsilon BZ}=\frac{\theta^{\epsilon}}{e^{\epsilon A}}$$

and equation (21) may be written

$$H=\frac{M\theta^{\epsilon}}{e^{\epsilon A}}+Z+\frac{1-\epsilon}{\epsilon B} \qquad (22)$$

Let θ_1 H_1 Z_1 refer to the initial state, the starting point of the expansion line, and let

$$\frac{M\theta_1^\epsilon}{e^{\epsilon A}} = H_1 - Z_1 - \frac{1-\epsilon}{\epsilon B} = L \tag{23}$$

Then equation (22) takes the form

$$H = L\left(\frac{\theta}{\theta_1}\right)^\epsilon + Z + \frac{1-\epsilon}{\epsilon B} \tag{24}$$

and the heat-drop along the expansion line between two points at the absolute temperatures θ_1 and θ_2 is given by

$$H_1 - H_2 = Z_1 - Z_2 + L\left[1 - \left(\frac{\theta_2}{\theta_1}\right)^\epsilon\right] \tag{25}$$

For isentropic expansion $\epsilon = 1$. Hence by setting $\epsilon = 1$ in equations (22), (23), and (24) we have, along the isentropic through the starting point of the expansion line,

$$H = N\frac{\theta}{\theta_1} + Z \tag{26}$$

where

$$N = H_1 - Z_1 \tag{27}$$

and the isentropic heat-drop from the initial point at $\theta = \theta_1$ to the final pressure where $\theta = \theta_2$ is given by

$$H_1 - H_2 = Z_1 - Z_2 + N\left(1 - \frac{\theta_2}{\theta_1}\right) \tag{28}$$

The reheat factor therefore has the value

$$R = \frac{Z_1 - Z_2 + L\left[1 - \left(\frac{\theta_2}{\theta_1}\right)^\epsilon\right]}{\epsilon\left[Z_1 - Z_2 + N\left(1 - \frac{\theta_2}{\theta_1}\right)\right]} \tag{D}$$

in which

$$N = H_1 - Z_1 \tag{D$_1$}$$

$$L = N - \frac{1-\epsilon}{\epsilon B} \tag{D$_2$}$$

Beside necessitating our working with absolute temperatures, the determination of R by equation (D) requires our finding the values of Z_1 and Z_2 either graphically or by computation from equation (13). As a means for the practical computation of R for use in designing, equation (D) is evidently so inconvenient as to be entirely worthless; but it has a value as confirmatory of the results obtained by the practical rule given in section 11; for it has been shown that that rule gives sensibly the same results, within the range of present steam-turbine practice, as equation (A), and furthermore that equation (D), based on a much more accurate assumption than that which underlies the deduction of (A), must give more accurate values than (A) and therefore than the rule. If, therefore, equation (D) gives sensibly the *same* values as the rule, the values obtained by the rule mav be relied upon as sensibly correct.

14. TESTS OF THE RULE FOR FINDING THE VALUE OF R

The tests consisted in computing R by equation (D) and comparing the results with values obtained by the rule given in in section 11.

The values of Z read from the $H\ \varphi$ chart at $\varphi = 1.384$ were plotted against $log_{10}\ \theta$ and a straight line drawn through the points; the scales were 100 B. t. u. = 75 mm and, for $log_{10}\ \theta$, 1.5 mm = 0.01. The values of Z_1 and Z_2 needed in the computations were read from this plot. The slope of this line when reduced to terms of naperian logarithms for use in equation (D_2) gave $1/B = 723$. The readings of H_1 for use in equation (D_1) were made from the $H\ \varphi$ chart. More exact results might have been had by obtaining all these values by computation instead of graphically, but the precision of the graphical method is sufficient for our purpose. It will not do, however, to compute H_1 from the table, but take Z_1 and Z_2 from a plot or from an equation derived from readings on the chart, for considerable errors are thereby introduced. The chart, while self-consistent and quite accurate enough for all ordinary purposes, is not an exact representation of the tables, owing doubtless to difficulties in printing. This, however, need not occasion any lack of confidence in the chart, for the test of its accuracy is a severe one, as will be found upon making a few computations by means of equations (D), (D_1), and (D_2).

A number of test computations covering the part of the saturation field, which is of practical importance, were made by the foregoing method. Values of R for the same cases were computed by the rule of section 11 and in many instances also by equation (A). On the whole the values obtained by the rule agreed with those obtained by the use of equation (D) somewhat more closely than did values from equation (A). A summary of the results of these tests is given in the following table:

TABLE III

Value of ϵ × [R by equ. (22) − R by rule] expressed as percentage of $(H_1 - H_2)$

$\frac{p_1}{p_2}$	p_1 lbs/in² abs	x_1	ϵ=0.1	ϵ=0.2	ϵ=0.4	ϵ=0.6	ϵ=0.7
12.7	277.4	0.981		+0.03	−0.02	−0.02	
45.5	277.4	.981		+ .04	− .09	− .10	
185.0	277.4	.981		− .03	− .20	− .22	
44.0	66.2	1.00		− .06	− .09	− .10	
33.7	21.9	.99		+ .04	− .04	+ .05	
33.7	21.9	.88		+ .04	− .06	+ .07	
33.7	21.9	.77		+ .06	+ .07	− .08	
20.0	20.0	.99	+0.04		− .01		+0.03
20.0	20.0	.84	+ .04		+ .04		− .02
20.0	20.0	.79	+ .04		− .02		− .01
20.0	120.0	.99	+ .07	+ .05	+ .03		+ .04
20.0	120.0	.84	+ .08	+ .04	+ .03		+ .04
300.0	300.0	1.00		− .01	− .19	− .25	
110.0	110.0	1.00		− .06	− .13	− .10	
35.0	35.0	1.00		+ .07	+ .01	− .01	
8.0	8.0	1.00		+ .03	+ .01	+ .02	

In the first three columns of the table are given the pressure ratio, the initial pressure, and the initial dryness factor; and it will be seen that the tests are sufficiently varied.

The object in using the reheat factor is to determine the position of a point B with an error in vertical position which shall be negligible in comparison with the isentropic heat drop $(H_1 - H_2)$. This difference of position, in percentage of $(H_1 - H_2)$, is found by multiplying the difference of the two values of R—found by the two methods—by the value of ϵ, since R is always nearly unity. Accordingly, the values in the table may be regarded as the changes of height of the point B, in per cent of $(H_1 - H_2)$, caused by changing the method of computing R. The positive sign means that the rule gives B a higher position than it should have according to equation (D).

On account of errors in reading H, Z, and $R-1$ from the curves, differences of less than 0.1 have little or no significance unless p_1/p_2 is very large. It will be seen that the discrepancy never exceeds one-fourth of 1 per cent and attains the value 0.1 per cent only when the pressure ratio is large.

Since one-fourth of 1 per cent is, for the designer, a negligible quantity, we may conclude that since one of the methods certainly gives a much more accurate value than the other, the error involved in either method is negligible and the value of R is accurate enough when found in either way. It follows that the values of R obtained by the working rule given in section 11 may be relied upon *for wet steam* as being sufficiently accurate for use in designing.

15. USES OF THE REHEAT FACTOR

Having thus a practical method of finding the reheat factor, we are able to plot the expansion line. If p_1 and p_2 are the terminal pressures, the position of the final point may be found by the equation

$$H_1-H_2=R\epsilon\ (H_1-H_3) \tag{29}$$

We next take, instead of p_2, the pressure corresponding to some isopiestic about halfway (on the diagram, not numerically) between the two terminal isopiestics. Using the rule to find R for expansion from the initial to this intermediate pressure, we compute the position of a point on the expansion line where it intersects this intermediate isopiestic. Having now three points of the expansion line, we may sketch it in as a circular arc. It will then be evident whether or not it is worth while to go on to determine still more points. Unless the expansion ratio p_1/p_2 is large, even a single intermediate point will usually be needless and, after the final point B has been found, a straight line AB will be close enough to the true expansion line, even in the middle. This, however, is a matter for the discretion of the individual designer, who knows what reliance he may place on the value of the stage efficiency on which his work is based.

In designing a turbine for new conditions, it may be worth while to make a number of preliminary sketch designs which need not be worked out in detail further than to compute the probable influence on the water rate of variations in the arrangement of the stages. In such work, what is needed is not the form of the expansion line but merely the actual heat drop $(H_1 - H_2)$, which may be expected in a given set of similar stages. If the expansion ratio is large, neglecting the reheat factor may introduce an error of 5 per cent or more, which is undesirable and may be avoided by a single computation of the reheat factor for use in equation (29).

16. GENERAL REMARKS

The foregoing methods are valid only when the isopiestics are straight lines; they therefore fail for superheated steam. The curvature of the isopiestics in the superheat field depends on the specific heat of superheated steam at constant pressure. Even if this were exactly known and expressible in simple mathematical form, the development of a general differential equation for the expansion line would be a difficult matter and the task of integrating it would very possibly present insuperable mathematical difficulties. But without attempting this general solution a few pertinent remarks may be made.

(*a*) Consideration of the $H\varphi$ chart shows that an isentropic expansion between two given isopiestics involves a greater change in temperature for superheated than for wet steam, as may also be seen from the pv chart. A dissipative expansion line starting at a point in the superheat field will therefore fall more sharply at first than if it started at the same pressure within the saturation field and the reheat factor for a given pair of terminal pressures and given stage efficiency will be greater than for wet steam between the same pressures. Hence, if we use the value of R computed for these pressures for wet steam, we shall underestimate the actual heat-drop and combined efficiency and be on the safe side as regards the economy expected.

(*b*) Up to 100° F superheat the curvature of the isopiestics is so small that the error can at most not be important if we simply use the value of R for wet steam between the same pressure limits.

(*c*) The value of the quantity $(R-1)$ decreases with the pressure ratio p_1/p_2 and decreases as the stage efficiency ϵ increases. Examination of the $H\varphi$ chart in connection with Table II shows that, unless the efficiency is very poor, with superheats up to 150° or 200° F, which are unusual as yet, the expansion ratio, and therefore $(R-1)$, can not be large for expansion entirely within the superheat field, so that $(R-1)$ can not be subject to a large error. With poor efficiency the reheat might be enough to keep the steam dry a long way down in the turbine, but such a case is not of great commercial interest and does not demand close designing.

(*d*) A high initial superheat has not as yet been much used in the Parsons type of turbine, so that the superheat field is of interest mainly to the designer of turbines in which the first few stages, at least, are of the impulse type, not requiring fine radial clearances. In such a turbine, the first one or two stages will usually have rather large pressure ratios and will get rid of the superheat, so that the remaining stages are working with wet steam. It is not a serious matter to treat one or two stages separately, by determining the state-points graphically, and it is usually necessary to do so for at least one stage. For the first stage is usually not quite like the later stages and has not the same stage efficiency, so that an expansion line drawn for constant stage efficiency could not fit the facts in any event.

(*e*) The whole idea of the reheat factor and the need of drawing the expansion line arises from the fact that the combined efficiency of a number of similar stages in series is greater than the efficiency of each stage separately. The method developed for finding the reheat factor was based on the assumption that the heat-drop in each stage was small, for it consisted in developing and integrating a *differential* equation for the expansion line. For a few stages with very high steam velocities, the results would not be exact, but the whole matter is also, in that case, of no importance; for the graphical construction for a few stages is a simple operation and involves no great waste of time.

(*f*) The notion of a reheat factor, as the term has been used in this paper, is not applicable to a single stage. Let p_1 and p_2 be the limiting pressures of a given single stage, and A (Fig. 9) the initial state.

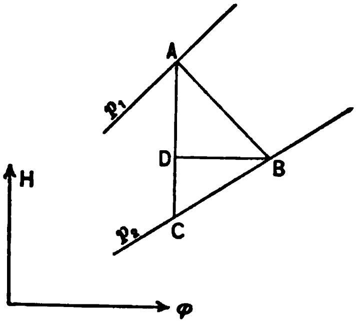


Fig. 9

Then if B is the final state

$$\frac{\overline{AD}}{\overline{AC}}=\frac{H_1-H_2}{H_1-H_3}$$

is the ratio of the mechanical energy produced to the maximum possible in adiabatic expansion. If, as may be assumed in an impulse stage, the difference of kinetic energy between similarly situated points is negligible, $\overline{AD}/\overline{AC}=\epsilon$ is the efficiency of the stage. This is true regardless of whether the isopiestics are straight or curved, i. e., whether the steam is wet or superheated, so long as B is at p_2, AC is vertical and DB is horizontal. If the net efficiency of the stage is given beforehand, B is thus fixed by the initial state A and the final pressure p_2 and there is no question of a reheat factor.

But the efficiency ϵ may have been obtained in either of two ways. If it was obtained by experiments on a stage similar to the one in question and working under similar conditions, there is nothing more to be said. But if it was computed from a velocity diagram drawn with proper allowances for velocity losses in nozzles and blades, with subsequent correction for windage and leakage, the case may be a trifle different in theory though hardly in practice.

Let A and therefore C be given, and let D be so placed as to make $\overline{AD}/\overline{AC}=\epsilon$, where ϵ is the computed efficiency. It now becomes a question of when the various elements of the total dissipation occur and of the temperature of the steam when the various elements of the reheat are added to it. In an impulse stage, in general, only a small fraction of the dissipation occurs in the nozzles, hence the reheat is almost all added to the steam after the lowest pressure and temperature have been reached. The actual expansion line is therefore nearly coincident with the broken line ACB, which would be the expansion line if *all* the dissipation and reheating took place at p_2. Hence, if ϵ were computed by some method which treated the reheat as *all* added at the low pressure, while in reality a little of it is added at a higher pressure and temperature in the nozzles, the efficiency thus computed would be a trifle too small and should be multiplied by a factor analogous to the reheat factor which, in effect, is introduced to allow for the fact that in a series of stages the reheat is distributed instead of being concentrated at the end of the last stage. The improvement in accuracy due to the use of such a factor would, however, be altogether illusory until our experimental knowledge is sufficient to permit of a far more accurate *a priori* computation of the stage efficiency than is at present possible.

To apply a reheat factor computed for the case of continuous expansion through an infinite number of stages, to expansion between the same pressure limits through a single stage, is altogether erroneous.

(*g*) In conclusion we may say that, so far as present practice is concerned, the fact the method given in this paper for finding the value of the reheat factor is applicable only to wet steam, is not an important restriction on its usefulness. In the designing of turbines with many similar stages, its use may save a great deal of time that would otherwise have to be spent over the drawing board.

NOTE (TO SEC. 1).—LIMITATIONS OF THE THEORY

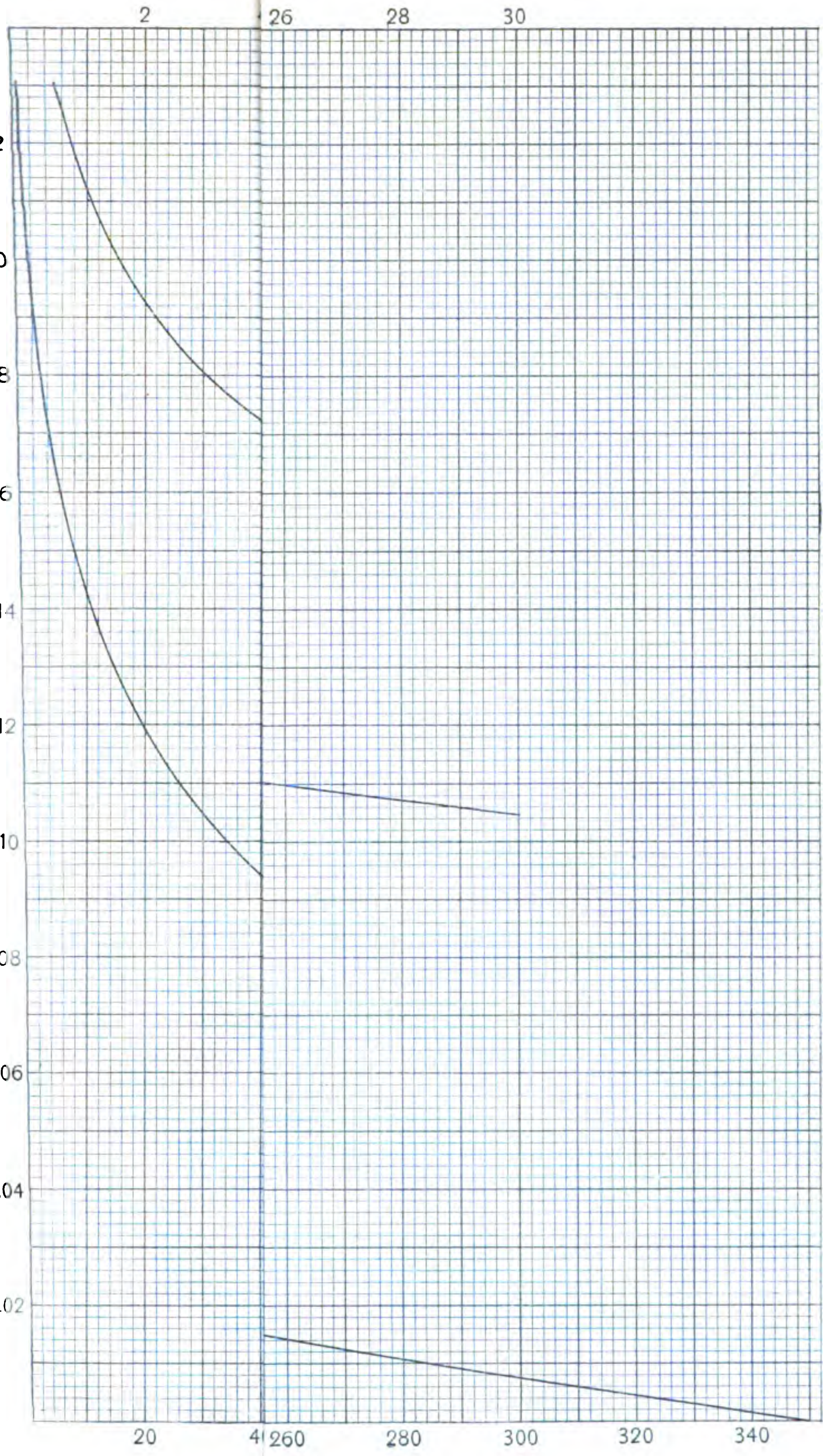
In the total energy equation, the terms T_0 and T are taken as including only kinetic energy of the axial component of the velocity of the fluid. This is done because the only kinetic energy which can be utilized mechanically is that due to the general motion of the fluid as a whole. Kinetic energy which is not utilizable, such as that of eddy currents, is for our purposes not to be counted as "mechanical" energy. It must ultimately be dissipated into heat; and motions which are already so unordered as to be incapable of mechanical utilization may be considered as already, for our purposes, completely dissipated. It is of no importance to the practical theory of steam flow whether they have already become completely unordered in the molecular sense or not.

A question then arises as to what is meant by the "state" of a mass of fluid when it is the seat of eddy currents which are still on a relatively large scale though already beyond our power to utilize their kinetic energy directly. In going on to complete dissipation, they "produce heat," which is merely our convenient way of saying that the dissipation tends to raise the temperature of the fluid. We are thus led to ask precisely what is meant by the temperature of the fluid at a given point in its course, and a very little consideration at once makes it clear that the "state" of a mass of fluid can not be precisely defined at all, unless it is a state of quiescence. Turbulent states are not capable of precise description, and the terms pressure and temperature have no *precise* meaning when referring to a fluid in a condition of turbulent motion nor even when referring to a volume element of a fluid moving as a whole with a rapid acceleration.

But though the *precise* treatment of the vastly complicated process of steam flow through a turbine is quite beyond our powers, the only important question is whether our theory is nearly enough correct for practical purposes—whether it represents the facts sufficiently well to be useful in predicting what will happen practically in a future case. This question may without hesitation be answered affirmatively. We neglect certain recognized errors in the theory and while we can not say, a priori, just how large these errors are, we find a posteriori that they are negligible if we use the theory with good judgment and do not throw common sense to the winds. If one attempted to measure the temperature of the steam issuing from a de Laval nozzle by putting the bulb of a mercurial thermometer directly in the jet, and then—assuming that the thermometer could endure such treatment—compared the readings with the theory, one might find very large discrepancies. But no sensible person would expect anything else.

Every physical theory is built upon a simplified ideal picture of the main outlines of the known facts. The simplifications, when recognized, constitute the assumptions or hypotheses stated as a basis for the theory. The degree of simplification permissible depends on the accuracy expected in using the theory for prediction and is limited by the accuracy attainable in the experimental verification of the results of prediction. In these respects the theory of the steam turbine does not differ at all from other physical theories; only it happens that the accuracy required of the theory is low on account of experimental difficulties, and that the things which the theory neglects in making its ideal picture of the facts are so obvious that anyone can see them.

WASHINGTON, March 2, 1911.



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RADIOMETRIC INVESTIGATION OF WATER OF CRYSTALLIZATION, LIGHT FILTERS, AND STANDARD ABSORPTION BANDS

By W. W. Coblentz

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I. INTRODUCTION

Although investigations of infra-red absorption spectra were begun about 25 years ago, it was not until the first years of the present century that an attempt was made to systematize the data previously obtained, and to publish it, as well as new data, in standard wave lengths. This was due in part to the lack of knowledge of the optical constants (which precluded the calibration) of the prisms used and to the difficulty in operating the spectroradiometric apparatus. To some the data seemed to be of interest, but of no great utilitarian value. To others the data seemed useless because of the question of the purity of the material used and because of their not recognizing that the absorption spectrum of the impurity will be weak and will be superposed upon that of the substance in question.

The early experimenters were at variance as to whether the cause of the absorption bands is an inter- or intra-molecular phenomenon. If the cause is intra-molecular, then it ought to be possible to identify certain characteristic absorption bands with specific groups of atoms or radicals in the compound under investigation. Now, in the study of the carbon compounds their constitution has been established by the replacement of certain constituents by organic radicals, by the preparation of a series of derivatives, by vapor density determinations, or by studying their physical properties in solution. Hence, following the example of the preceding experimenters, the writer turned to organic compounds for examples of substances having characteristic groups of atoms. Searching for further illustrations, groups of inorganic substances (e. g., sulphates and nitrates) were examined. The chemical formulæ of minerals appeared to be written with such exactness that this seemed a rich field for material. But it was soon found that in mineralogy it has as yet not been possible to apply any of the aforesaid methods used in organic chemistry, that the constitution of many minerals has been derived indirectly from analogies with other compounds which are better understood, and that in many cases the constitutional formulæ are in doubt.

Being familiar with the older ideas in regard to the condition of water in crystals, it seemed easy to settle the question of intermolecular action in causing absorption bands, by investigating substances containing *water of constitution* and *water of crystallization;* but at the very beginning[1] it was found that this particular subject was in a more hopeless state of confusion than all the rest.

In the meantime extensive investigations of all sorts of compounds proved conclusively that the important groups of elements, radicals, which are found in chemical compounds, have a definite effect upon radiant energy, especially upon low frequency or so-called infra-red radiation. This effect is manifested by intense absorption bands, the positions of which are characteristic of the radical or group of atoms causing these bands.

Hence as a result of the application of these facts it has come about that instead of turning to chemistry and to other branches of physics to obtain evidence to explain the phenomena observed when radiant energy is passed through or is reflected from a substance, the problem is reversed and these very phenomena are now applied to explain several conspicuous and intricate questions concerning the constitution of matter, and in particular the question of the manner in which water, or the constituents which form water, are combined in chemical compounds.

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[1] Coblentz: Physical Review, **20**, p. 252; 1905.

The investigation of water in minerals has been carried on at various times[2] during the past six years. It consisted in but little more than gathering data and publishing it, leaving to the future the practical applications.

The interest which Dr. Hillebrand has taken in this method of analysis has served to renew my interest in it and to further test its possibilities. After due consideration of the problem it was deemed best to renew the work by investigating opals having different amounts of water, from 3 to 8 per cent. After beginning the work it was found possible to decrease the water content of, and even to completely dehydrate, some specimens without seriously impairing their homogeneity. The material was selected from the collection in the United States National Museum. The water content was very kindly determined by Dr. Hillebrand, after which the cutting of the sections was done by the United States Geological Survey.

II. THE FUNCTION OF WATER IN SUBSTANCES

The manner in which *water of crystallization* is held in minerals is not understood. By some it is considered to belong to the molecular structure; by others it is held that the molecules of water belong only to the crystalline structure. It is a characteristic of water of crystallization that it is expelled from a mineral by very gentle ignition, always at a temperature far below red heat and frequently below 100° C.

In the case of *water of constitution*, the water is not supposed to exist as such in the mineral, but to result from the union of oxygen and hydrogen or from hydroxyl groups contained in the molecule. It is characteristic of this class of substances that they must be strongly heated, sometimes to a white heat, before they are decomposed and all the water is expelled.

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[2] Water of Constitution and Water of Crystallization, Phys. Rev., **20**, p. 252; 1905. Phys. Rev., **23**, p. 125; 1906. This Bulletin, **2**, p. 457; 1907. Jahrbuch f. Radioaktivität und Electronik, **8**, p. 397; 1907. Phys. Rev., **30**, p. 322; 1910. Publication No. 65, Carnegie Institution of Washington.

The earlier writers held that in the case of crystalline substances the molecules of water exist in their entirety, situated among the other molecules of the substance, whence the name *water of crystallization.*

"The compounds[8] containing water of crystallization are usually denied the title of atomic compounds, ordinarily applied to combinations of two or more elements in which the constituent atoms are associated in a single molecule, under the influence of the force which has received the name of chemical affinity, and in contradistinction are termed *molecular* compounds, being regarded as combinations of two or more separate molecules, e. g., $CaSO_4 + 2H_2O$. This, although perhaps true of many compounds containing water of crystallization, is certainly not true of all, and notably of some of the sulphates (e. g., $MgSO_4 + 7H_2O$), which are deprived of their water of crystallization by heating to a high temperature. The last molecule retained with such persistency was termed *water of constitution* to distinguish it from *water of crystallization.*

In the present state of our knowledge it is impossible absolutely to define the meaning of these terms, or even to say that there is an absolute difference between the so-called *water of crystallization* and *water of constitution*, and not merely one of degree."

In many compounds the affinity seems different for the different parts of the crystal water. For example, ordinary alum $AlK(SO_4)_2 + 12H_2O$ gives off five molecules of H_2O at 100°, and five molecules at 120°, while the last two molecules remain until heated to 200°. In the same manner in the sulphates of Mg, ($MgSO_4 + 7H_2O$), Zn, Fe, Ni, and Co six molecules of water are given off at about 130° while the last molecule of H_2O does not pass off until heated to 200° to 300° C. Examples of *water of constitution* are mica, and brucite, $Mg(OH)_2$, in which the O and

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[8] Encyclopædia Britannica, 9th ed., V, pp. 489, 505. See also Graham-Otto Lehrbuch der Chemie, II, p. 173.

H atoms are not united as H_2O, and do not unite to form water until sufficient heat is applied.

In cases where successive portions of water are given off at different temperatures it is difficult to make a distinction between water of crystallization and water of constitution. In the minerals just quoted it has been found that the heat of hydration of the last molecule of water is different from that of the molecules of water which pass off at a lower temperature, which confirms the belief of a difference in the bonding in the two cases.

Various other criteria have been set up (often based upon physical tests, refraction and polarization) by experimenters to distinguish between these various forms of water, but all seem unsatisfactory. For example, the fact that in certain crystals the water passes off at one, two, or three fixed temperatures, with a supposed change in homogeneity, has been considered evidence that the water is present as a definite compound. But the absorption and reflection bands of selenite ($CaSO_4 + 2H_2O$) show that it is a "double salt" or "molecular compound;" for the spectrum of selenite is the composite of the spectra of anhydrite $CaSO_4$, and of water, H_2O.[4] If selenite were a new compound, formed by the union of water and $CaSO_4$, then the (absorption and reflection) spectrum should be entirely different from that of the constituents, just as is true of mica. That some of these hypotheses are too limited is shown by the fact that the absorption spectra of various substances like selenite, opal, and the zeolites are identical as regards the position and intensity of the water bands. The water must therefore be present in the same manner in these two types of crystals; and since the absorption bands are identical with those of water in its free (liquid) state it would appear that the temperature fixed point and vapor pressure tests are not a sufficient criterion for judging this question. If the water were chemically combined in selenite, then one would expect to find the absorption bands of water to be absent. It would appear just as tenable to consider the water occluded under a definite pressure, which raises its boiling point to a higher temperature. [In this connection it would be interesting to investigate the expansion, with change in temperature, of crystals containing water of crystallization, to learn whether there is a minimum such as obtains in water at 4° C.] Or we may liken the crystal unto a block built up of bricks and mortar. This analogy can not extend very far, since an explanation is demanded why in the one case the cement (water) crumbles at a definite temperature while in other cases (zeolites) the phenomenon is progressive with rise in temperature.

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[4] This Bulletin, 2, p. 457; 1907. Carnegie Publication No. 65, pp. 18, 77, and 79.

That the hypothesis that water in crystals is united as a definite compound is based on a too narrow foundation is illustrated in the zeolites. They are crystalline compounds and the water is very loosely held. The water continues to be gradually expelled as the temperature is raised, and it may be replaced by other substances, such as NH_3, H_2S, or C_2H_5OH. The dehydrated crystals absorb definite quantities of these substances as a sponge absorbs water, the process being accompanied by the evolution of heat. Since the amount of water present varies continuously with the vapor pressure, it is generally concluded that the water in the zeolites is not analogous to the water of crystallization of most hydrated salts, but resembles more nearly the intermixture which occurs in solid solution. In this case the hypothesis is tenable, for amorphous substances, e. g. opal, which have similar absorption spectra, are also considered solid solutions; and in both groups of minerals the absorption spectrum of the hydrated material is the composite of water and of the anhydrous substance. But the vapor pressure criterion is not sufficient to judge minerals as may be noticed from the experiments on tremolite. Here, too, the water is expelled gradually [5] with rise in temperature and it was considered dissolved water; but no absorption bands of water are observable. The small bands at 2.9μ may be due to hydroxyl groups as inferred by Penfield and Stanley [6]; for in brucite $Mg(OH)_2$, in diaspore, $AlO(OH)$, and in göthite, $FeO(OH)$ the 3μ band is very weak [7], as is true of the band in tremolite.

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[5] Allen and Clement: Amer. Jour. Sci., **26**, p. 101; 1908.

[6] Penfield and Stanley: Amer. Jour. Sci., **23**, p. 23; 1907.

[7] Publication No. 65, Carnegie Institution of Washington. This Bulletin, **2**, p. 466; 1907.

Turning from the crystals (e. g. sulphates) which give off their water at one or more fixed temperatures to the zeolites, which are also crystalline substances, it is found as mentioned on a previous page, that in the latter group of minerals the water is given off gradually between 100° and about 400°. To explain this phenomenon it is supposed that the water is not chemically combined, but is present as solid solution. On this hypothesis the water should be present as such, and should give the absorption bands of water. As a matter of fact, as already mentioned, the zeolites do show the absorption bands of water; but so do the sulphates and other substances in which the water is expelled at a fixed temperature, indicating the sameness of the water in both groups. It is not clear to the writer why, if in some substances the water may be expelled at one fixed temperature and in another substance at several fixed temperatures, it is not possible to have still other crystalline structures from which the water may be expelled at all temperature gradations; and yet have the water present in the same condition in all of them, as indicated by the radiometric tests.

III. THE CRITERION USED IN THE PRESENT METHOD OF ANALYSIS

The criterion used in the present investigation for judging the condition of water in compounds is based upon the evidence deduced from extensive experimental data which shows that the absorption spectrum of a compound is *not* the composite of the absorption bands of the constituent elements. In this case the "physical molecule" has been changed. On the other hand, if the molecules (or the groups of atoms which cause the characteristic absorption bands) undergo no physical change when they combine to form a crystal (e. g., selenite, $CaSO_4 + 2H_2O$) or when they enter into solution, then the absorption spectrum of the resultant combination will be the composite of the absorption bands of the constituents. Now this is the proposition that conflicts with some of the notions concerning definite chemical compounds. From the fact that there is a certain heat of hydration manifested in the formation of a crystalline substance, e. g., hydrous sulphates, it is inferred that there is a new compound formed, when as a matter of fact the radiometric test shows that the water and the sulphate bands are just the same in magnitude and in position as they were before the constituents were united.

In judging the condition of water in minerals the main difficulty is in using substances which in the anhydrous state have no large absorption bands near the bands characteristic of water in its free, liquid, state. An excellent example is found in selenite, $CaSO_4 + 2H_2O$, which has an unusually large absorption band at 4.6μ. This seemed to throw doubt upon the adequacy of the radiometric test until after the examination of anhydrite, $CaSO_4$, and other anhydrous sulphates, when it was shown that this large absorption band is characteristic of the sulphates. In the same manner the presence of OH groups in cane sugar confuses matters at 3μ, so that the probability of cane sugar having a molecule of water of crystallization is based upon the evidence deduced from the presence of absorption bands at 1.5μ and 4.75μ which coincide with the water bands at these points. The evidence not being very strong in this case, the writer has never laid much stress upon it, in spite of the great similarity of the spectrum to that of other sugars having H_2O. In all the other examples previously described, the most superficial examination shows that the absorption bands of water in the various minerals are identical in magnitude and in position with those found in water in its free liquid state. Hence, in the present investigation, the criterion for distinguishing water of crystallization from water of constitution is the presence of absorption bands at 1.5, 2, 3, 4.75, and 6μ which is the location of the absorption bands of water. If there are no other absorption bands nearby, then the intensity of these bands will be found similar to those of water, viz., the bands at 1.5, 2, and 4.75μ will be weak while the bands at 3μ and 6μ will be very strong. Hydroxyl groups cause an absorption band at 3μ, hence not distinguishable when present with water. Furthermore, the evidence for OH groups is not so clear cut and definite as is found in water of crystallization. The intensity of the band seems to depend upon the activity of the OH group. For example, of the various hydroxides studied, the alcohols, etc., have a sharply defined band at 3μ while in brucite, $Mg(OH)_2$, and in several other minerals, the band at 3μ is almost if not entirely wanting. In the alcohols, etc., the OH is more active since its hydrogen is replacable by a metal (more acid), than the OH in brucite which is not replacable (more basic). Whether this is the true explanation of the phenomenon remains undetermined; and since the question of OH groups is of secondary importance in the present work, it need not be given further attention at present.

In passing it is of interest to note that substances containing the C=O group (aldehydes, ketones, acids, esters) have a very marked absorption band in the region of 5.8 to 5.9μ. Silicates, as well as quartz, have a very small absorption band in the region of 2.9μ, which is barely noticeable in the thin sections of minerals examined. Since the band is so weak, there is no danger of confusing it with the strong water band at 3μ in opals.

In contrast with the other criteria, the radiometric test of the condition of water in minerals gives far more consistent results in classifying certain minerals. It is to be noticed, however, that this method of analysis shows no distinction between water of crystallization, dissolved water, and water of solid solution. In its behavior toward radiant energy the molecule of water in crystals and in solid solution is identical with water in its free liquid state. This is, of course, in conflict with the commonly accepted notions concerning water of crystallization and water of solid solution; but it seems to be the only logical interpretation of the data obtained by the present method.

The main difficulty in this investigation is in obtaining substances which in the anhydrous state are free from absorption bands. This is practically impossible, since all substances have characteristic absorption spectra. Hence the best that one can do is to investigate various substances. Some give inconclusive evidence in one region of the spectrum, e. g., cane sugar at 3μ, while others confuse matters further in the infra-red, e. g., the sulphates at 4.55μ. Considered as a whole, however, the evidence is complete and convincing.

IV. THE LEAST THICKNESS OF WATER DETECTABLE RADIOMETRICALLY

This is about the first question asked in connection with the methods used in the present investigation.

On a subsequent page it will be shown that a given layer of water vapor is far more transparent than the same column when condensed into a liquid film, although the large absorption bands are found in both the liquid and in the vapor phase, the only difference being that of intensity. The film of water which is found on rock salt (prisms) does not cause absorption bands.

Whether the absorption bands of water are absent in substances which are more hydroscopic than rock salt (or in rock salt itself when exposed to very humid air) has not been determined. Furthermore, it must be shown that such a film of water is continuous.

It will be shown presently (see Figs. 6 and 7) that after dehydrating a certain sample of opal it absorbed water at the rate of about 0.06 per cent (see Fig. 7, B) per day. The various transmission curves are so widely separated that an increase in the water content amounting to one-third to one-fourth this value (or 0.02 per cent) could easily have been detected. The thickness of the section of opal was 0.105 mm; and if 0.02 per cent of it is water the equivalent layer of water, if concentrated into a liquid film, would be about 3/100,000 mm in thickness.

V. APPARATUS AND METHODS USED

The apparatus used in the present investigation is essentially the same as used in previous work. The spectrum was produced by means of a 60° fluorite prism mounted on a spectrometer made of silvered mirrors 50 cm in focal length. The spectrum was explored by means of a very sensitive vacuum bolometer, which is now being used in all radiation work requiring high precision. The complete period of the auxiliary galvanometer was only 4 seconds, which means a great saving in time when one considers that in some of the earlier work 1 to 1.5 minutes were required to make a single observation. The spectrometer slit and the width of the bolometer were 0.6 mm wide or 4′ arc. A Nernst glower was used as a source of energy. An image of the glower was projected upon the spectrometer slit by means of a 15-cm focal length silvered mirror. The crystal section was mounted in a holder directly in front of the spectrometer slit. The methods of observation consisted in (1) noting the galvanometer deflection when the crystal section was in the path of the light from the glower, and (2) noting the galvanometer deflection when the crystal section was not before the spectrometer slit. The ratio of (1) ÷ (2) gives the transmission in any given part of the spectrum, and it is simply a matter of setting the bolometer in different parts of the spectrum and noting the two galvanometer deflections. The method is analogous to spectrophotometric measurements, the bolometer being substituted for the eye. An accuracy of 1 part in 200 to 400 is easily attainable, which is more precise than is required.

The mineral sections were ground thin but not highly polished. The size of the specimens was about 8 by 15 mm. They were mounted upon thick cardboard having rectangular openings cut therein. In this manner no light reached the spectrometer slit, except that which passed through the mineral section.

For further details in regard to apparatus and methods of observation the reader is referred to previous investigations of a similar nature.[8]

VI. SUMMARY OF PREVIOUS DATA

In previous investigations of at least 34 substances, said to contain "water of crystallization," the one exception (aside from tremolite which is included in the present paper) to the rule that such substances show the absorption bands of water was brucine, $C_{23}H_{26}N_2O_4+4H_2O$, which is an alkaloid having a complicated and unknown structure. An extensive examination of this compound failed to reveal any absorption bands of water. The transmission curve[9] has sharp bands at 1.7, 3.43, 6.86, and 7.3μ which are to be found in all substances containing CH_2 and CH_3 groups. It has also a very large band at 5.95μ (and 8.3μ) which is to be found in all substances containing the $C=O$ group. It is quite transparent throughout the infra-red. It is supposed to contain 16 per cent of crystal water which would be sufficient to cause a far greater opacity than was observed radiometrically.

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[8] Physical Rev., **16**, p. 35; 1903. Publication, Carnegie Institution No. 35, 1905; No. 97, 1908. This Bulletin, **4**, p. 392; 1907.

[9] Publication No. 65, p. 40, Carnegie Institution of Washington.

The list of minerals containing water of constitution included about a dozen samples of hydroxides (OH groups). As stated elsewhere, the absorption band of OH groups, which is so characteristic of alcohols at 3μ, is often very weak and sometimes it is entirely unresolved by the spectroscope. In serpentine there is a band at 3μ which is very strong, and confirms the view that there are hydroxyl groups present in this mineral. The radiometric analysis also confirmed the view[10] that there are no hydroxyl groups in talc, in which there is not even a trace of an absorption band at 3μ.

The one exception to the other methods of classifying the 28 substances examined, containing water of constitution, was cane sugar which is not supposed to have water of crystallization. As mentioned on a previous page, the evidence is not very strong; but there is sufficient similarity between the transmission spectrum of cane sugar and of other sugars having water of crystallization (no similarity with fructose which has no crystal water) to suggest the presence of a molecule of water of crystallization.

It seems rather remarkable that out of a sum total of more than 60 substances examined radiometrically only two (perhaps only one) were found which did not agree with the other classification into water of crystallization and water of constitution.

VII. NEW EXPERIMENTAL DATA

GROUP 1. MINERALS CONTAINING WATER OF CRYSTALLIZATION

Under this heading are described the characteristics of several crystalline and amorphous substances containing water. For, as already mentioned, the radiometric test finds no distinction between water of crystallization, absorbed water, or water in solid solution.

Water, H_2O.—In order to appreciate fully the significance of the data to be presented on minerals, it is necessary to describe the characteristics of water when examined in the liquid and in the

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[10] Clarke and Schneider: Amer. Jour. Sci., **40**, p. 308; 1890.

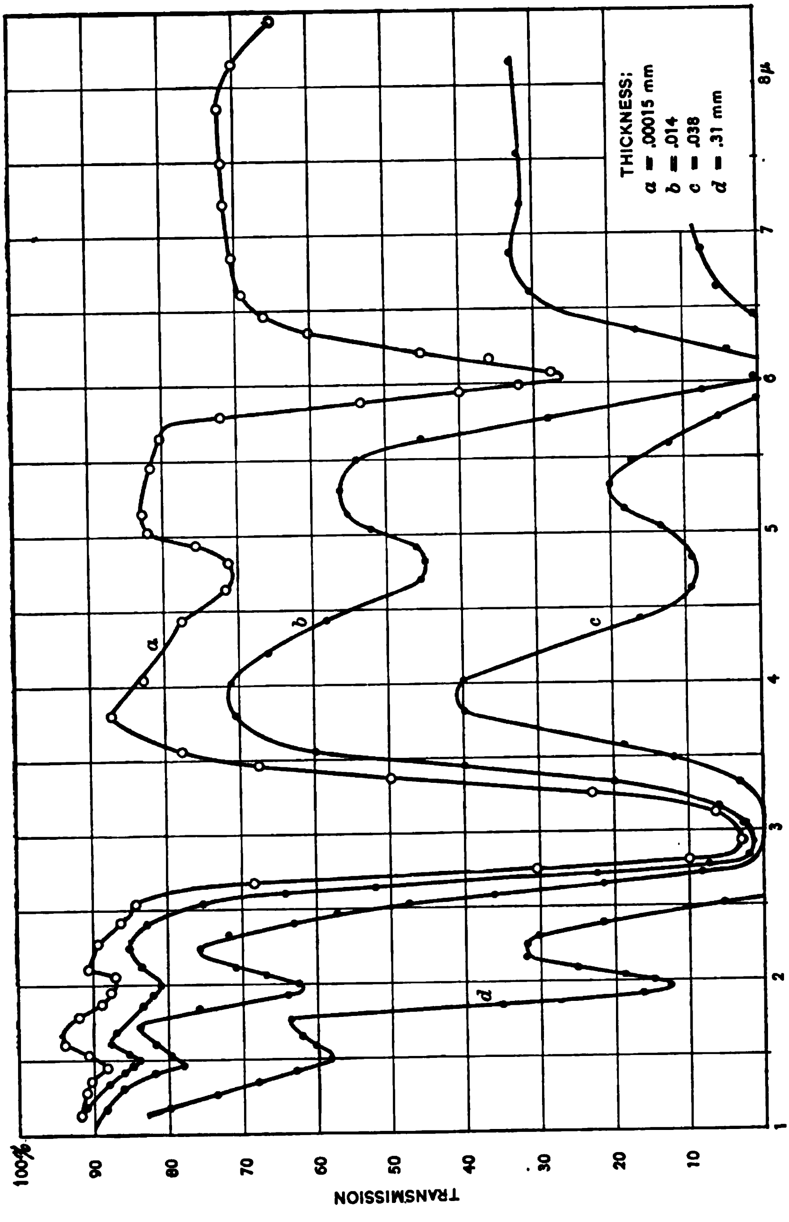

Fig. 1.—Water, H_2O

vapor state. All observers[11] agree in their location of large absorption bands of water at the approximate wave lengths 1.5, 2, 3, 4.75, and 6μ All have found that water is extremely opaque to the deep infra-red radiation, so that the film had to be reduced to a few thousandths of a millimeter in thickness in order to be able to study it at all.

In fact, of all the substances examined, which includes all the great groups of chemically related compounds, water stands unique in having a spectrum of numerous narrow absorption bands, which can be resolved only when the substance is reduced to a highly attenuated vapor. In the liquid state these groups of small bands coalesce into large bands as indicated in figure 1. It is of course well known that a very thick layer of water is required to produce absorption in the visible spectrum.[12] The same is true for the infra-red region out to 0.933μ (the "ρ" band in Fig. 2) but beyond this point the "general absorption" increases very rapidly, so that a layer of water 1 cm in thickness absorbs all frequencies beyond 1.4μ, and a layer 0.5 mm in thickness causes complete opacity beyond 2μ. The absorption of water for heat waves longer than 5μ is so much greater than at 2μ that a layer only 0.1 mm in thickness causes complete opacity beyond 5μ. Beyond 8μ to about 50μ water is quite transparent, having no large absorption bands which would be useful in investigating the present problem.

The transmission curves of various thicknesses of water ($a=0.00015$ mm; $b=0.014$ mm; $c=0.038$ mm; $d=0.31$ mm) are given in figure 1. The cell, containing water, was made of two large, clear fluorite plates separated by tinfoil. The various thicknesses were obtained by varying the number of layers of tinfoil. For curve *a*, the thinnest obtainable platinum, used in making bolometers, was inserted between the fluorite plates. The thickness of the platinum was computed from the electrical resistance and the surface dimensions of a bolometer strip. These curves show the great opacity of water at 6μ as compared with the region of 1.5 and 2μ.

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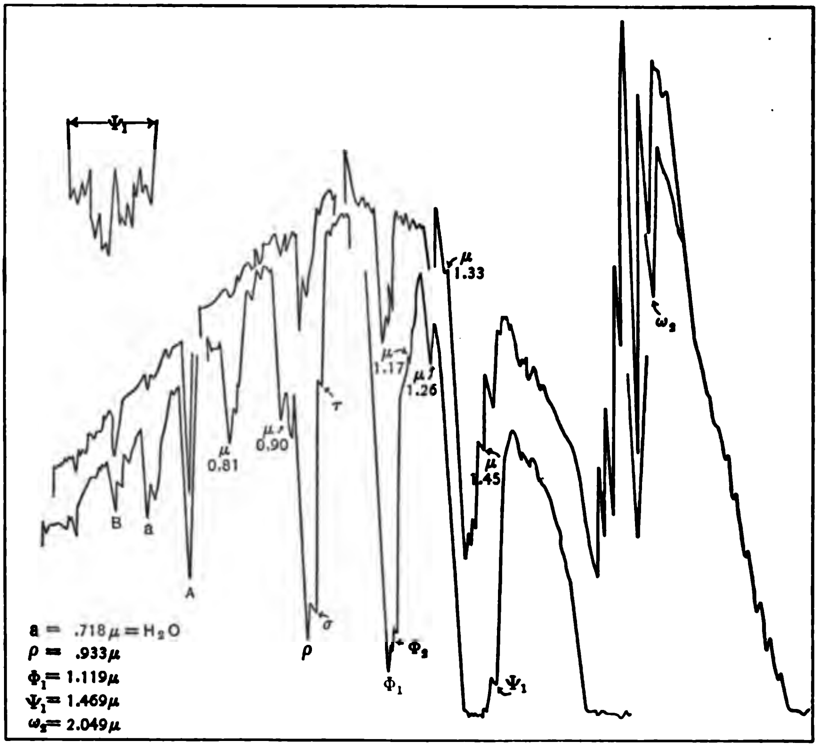
[11] Julius: Verhandl. Königl. Akad. Amsterdam, Deel I, No. 1, 1892. Paschen: Ann. der Phys. (3), **58**, p. 334; 1894. Aschkinass: Ann. der Phys. (3), **55**, p. 406; 1905.

[12] Abney and Festing: Phil. Trans., **172**, p. 887; 1882. Kayser: Spectroscopie, vols. 2 and 5.

Ångström[13] has shown that water vapor is more transparent than the liquid phase, when in such layers that the thickness is inversely proportional to the density. A familiar example is atmospheric water vapor which transmits the sun's radiation[14] to 11μ, while a layer of water 2.85 centimeters thick, which is equivalent to the water vapor in the earth's atmosphere (see Arrhenius Lehrb. der Kosmischen Physik, p. 630) absorbs everything beyond 1.2μ. The complexity of the absorption bands at 1.45μ and at 2μ, in figure 1, is shown in the spectrobolographic curves[15] made at the



BOLOGRAPHIC ENERGY CURVES OF THE SOLAR SPECTRUM OF A 60° GLASS PRISM

Fig. 2

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[13] Ångström: Ann. der Phys. (3), **39**, p. 267, 1890; (4) **6**, p. 163, 1901.

[14] Langley: Nat. Acad. Sci., **4**, pt. 2, p. 197. Discussion in Carnegie Publication No. 97, p. 143.

[15] Fowle: Smithsonian Misc. Coll., vol. 47, No. 1468; 1904.

Astrophysical Observatory. These curves are reproduced in figure 2. The upper curve, for February 19, 1903, was made when there was but small water-vapor absorption. The lower curve, for September 14, 1903, was made when the humidity was high, and hence there was great water-vapor absorption. The rapid variation in intensity of the absorption bands is analogous to the observations in figure 1. A further illustration of the complexity of the water bands is given in figure 3, which relates to the band at 6μ in figure 1. Curve *a*, figure 3, was obtained by placing a Nernst glower at a distance of 4.2 meters from the spectrobolometer and projecting an image of the glower upon the spectrometer slit by means of a large concave mirror. The spectral energy curve was then observed in the usual manner. When plotted to scale as shown in curve *a*, figure 3, the energy curve shows numerous indentations. The dotted line represents roughly the spectral energy curve of the glower if there were no absorption bands. By taking the ratio of the ordinates of the continuous part of curve *a*, to the dotted curve, at various wave lengths, curve *b* is obtained. The latter represents very closely the transmission of 4.2 meters of air, which contains a layer of precipitable water equal to 0.02 mm in thickness. The water content was derived from the relative humidity (=25 per cent; room temperature = 21.7°) and the amount of water vapor per cubic meter. It is to be noticed that the 6μ band which shows complete opacity for a similar layer of liquid, curve *b*, figure 1, is resolved into at least six bands with maxima at 5.75, 5.91, 6.05, 6.15, 6.41, and 6.56μ. The short air column used, 4.2 m, was not sufficient to show the absorption bands of water vapor at 3μ.

Anhydrite, $CaSO_4$.—The substance examined was a cleavage piece, split parallel to the *c* axis; thickness = 0.656 mm.

The transmission curve, *c*, figure 4, of this mineral shows small absorption bands at 3.75, 5.75, 6.15, and 6.55μ; a very large band, at 4.55μ, is characteristic of sulphates. This mineral was investigated previously, and is included here to illustrate the great difference in the opacity of the hydrous and the anhydrous mineral. (See curves *a* and *c*, in which the samples have practically the same thickness.)

Selenite, $CaSO_4 + 2H_2O$.—The sections examined were cleavage pieces split parallel to the *b* axis; the thicknesses being $a = 0.648$ mm, $b = 0.093$ mm, respectively. Since 21 per cent of selenite is water, the thickness of the water if free would be 48.8 per cent (sp. gr. of selenite is 2.33; $2.33 \times 21 = 48.8$) of the thickness of the specimen, or $a = 0.317$ mm and $b = 0.046$ mm of water.

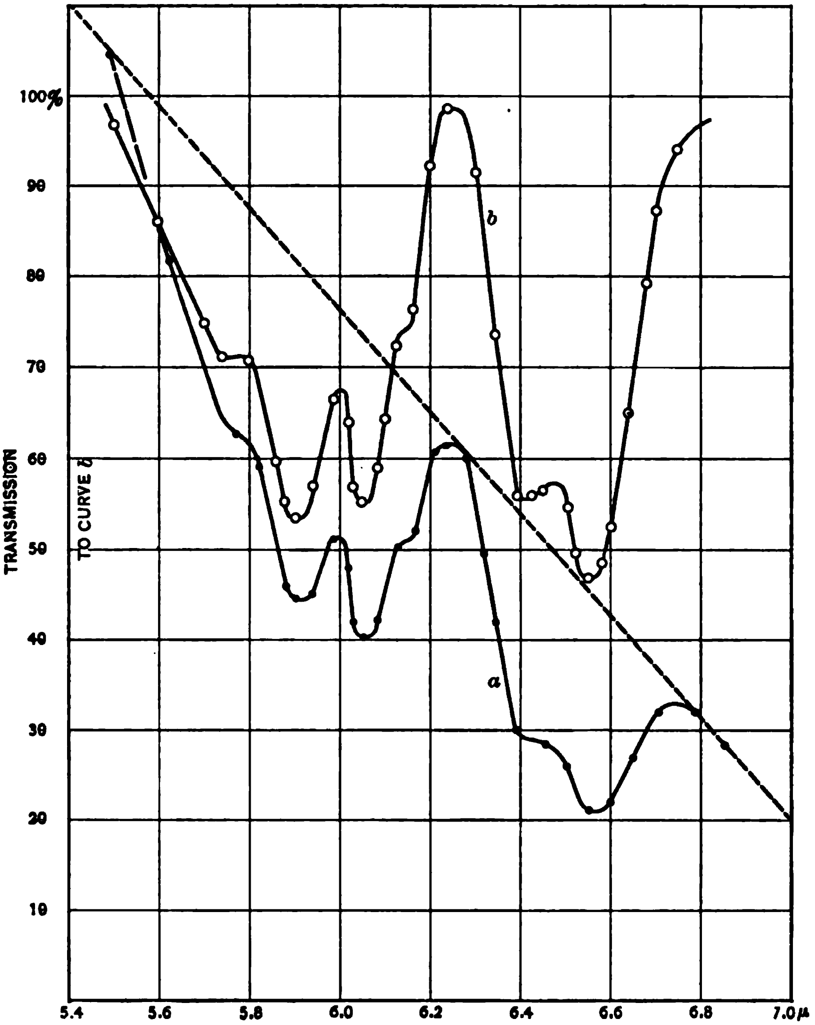

Fig. 3.—*Atmospheric Water Vapor*

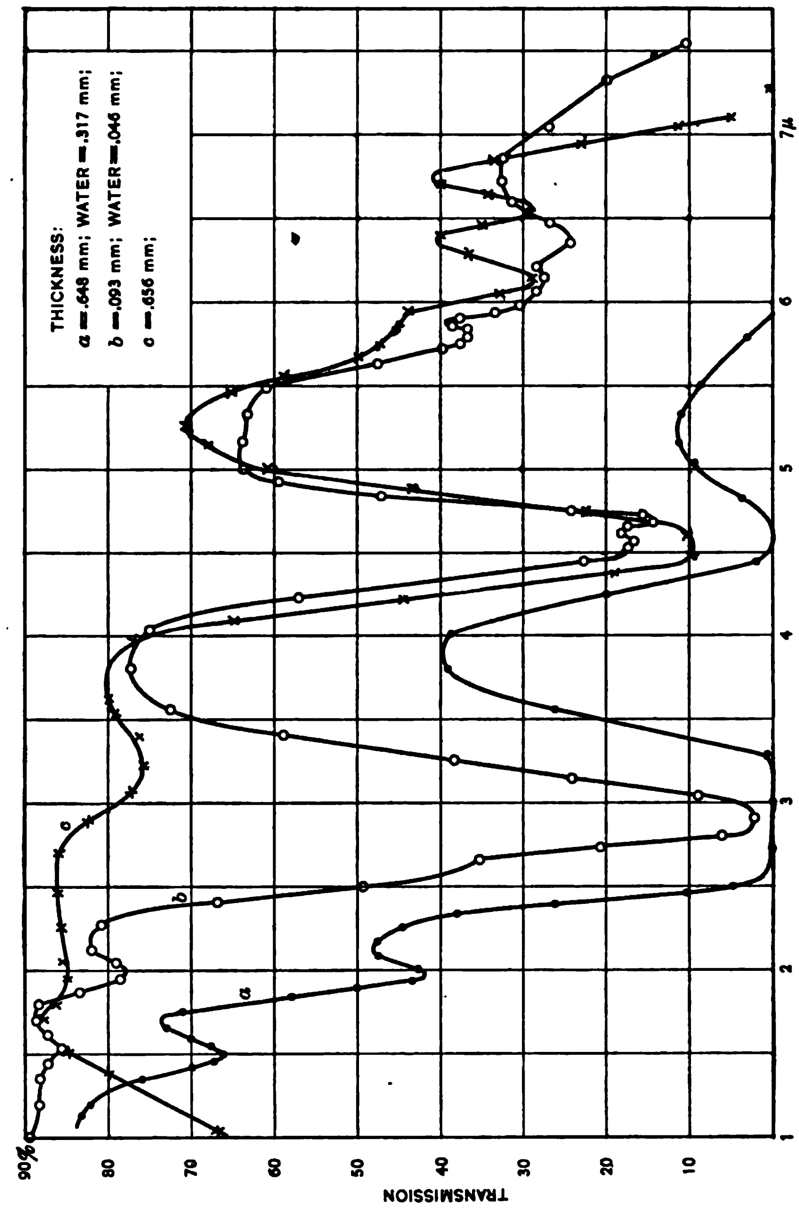

Fig. 4.—*Selenite,* $CaSO_4+2H_2O$ (*curves a and b*); *Anhydrite,* $CaSO_4$

Of all the minerals investigated, containing water of crystallization, this and the following one are the most conspicuous for demonstrating the effect of water upon the absorption spectrum of substances. The absorption bands of water at 1.5; 2.0, 3, 4.75, 6.0, and 6.5μ are very conspicuous in spite of the anhydrite bands which confuse matters at 6μ. It is to be noticed that a layer of water in its free liquid state, curve *d*, figure 1, is far more opaque than an equivalent layer, curve *a*, figure 4, when held in a crystal. This is evident from the fact that the 0.31 mm layer of water is entirely opaque beyond 2.5μ. In fact, the transmission spectrum of selenite indicates the presence of water in more nearly the vapor state, in which it is possible to resolve the large bands into smaller ones—see figure 3. This change in density of water in the process of crystallization involves energy changes which may require consideration in connection with the question of thermal equilibrium in dehydration.

In previous investigations[16] partially and completely dehydrated, also rehydrated samples of selenite were examined, to which reference must be made in order to fully appreciate the bearing of this data upon the question of water of crystallization.

Opal, SiO_2+xH_2O.—Samples of opal and quartz have been examined previously.[16] Quartz has small absorption bands at 2.9, 4.35, 5.02, 5.3, 6.0, 6.26, and 6.65μ. The band at 2.9μ is barely observable in a section 0.1 mm in thickness. Curve *c*, figure 5, gives the transmission of a section 1.435 mm in thickness, cut perpendicular to the optic axis. The maximum lies at 2.88μ. This absorption band is so weak that it can not interfere with the water band at 3μ. The bands at 6 and at 6.26μ form a composite with the water band at 6μ, of which the maximum appears at 6.1μ. The group of atoms in quartz is very strong and maintains its characteristics, more or less sharply defined, in the various silicates investigated.

Opal, amorphous quartz, contains variable proportions (2 to 30 per cent) of water. It shows no traces of crystallization. It is considered a solid solution, for the water contained is a function of the vapor pressure.

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[16] This Bulletin, 2, p. 457; 1907. Carnegie Publication No. 65.

The transmission curve of opal has the general outline[18] of the curve for water and contains the bands of water at 1.5, 2, 3, 4.75, and 6μ. The latter is complex, as mentioned above.

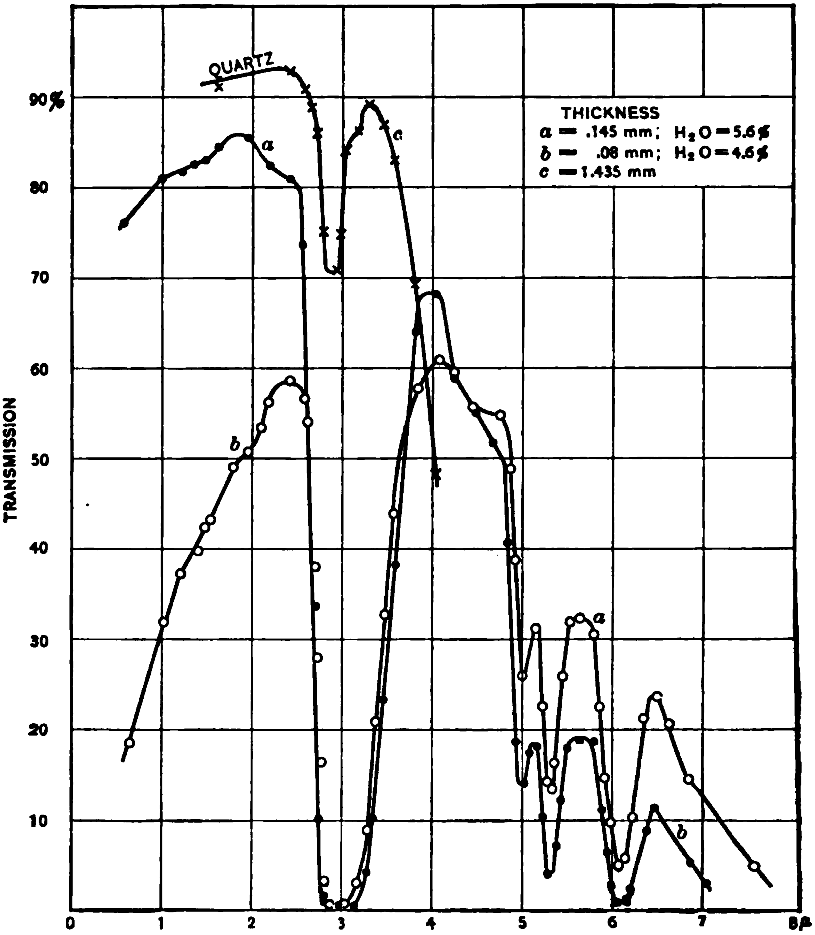

Fig. 5.—*Opal, SiO_2+xH_2O; Quartz, SiO_2*

For the present work the samples of opal were not perfectly transparent, which caused a scattering of the rays shorter than 2.5μ. In figure 5, curve *a* gives the transmission of a sample of opal (from Queretaro, Mexico) 0.145 mm in thickness, and containing 5.6 per cent of water. In transmitted light it showed a slightly milky white color which scatters the light to 2μ. Curve *b* gives the transmission of a whitish semitranslucent sample (from Silesia) 0.08 mm in thickness and containing 4.6 per cent of water. The equivalent layer of water for curve *a* is t = 0.018 mm, and for curve *b* it is t = 0.0077 mm. The rapid decrease in the general transmission beyond 4μ is due to the great opacity of quartz beyond 3μ.

In figure 6 is given, curve *a*, the transmission of a semitranslucent sample of opal, t = 0.105 mm in thickness, originally containing 3.6 per cent of water. The equivalent layer of water (sp. gr. of opal = 2.1) is 0.0079 mm. It was found possible to dehydrate the specimen without seriously increasing the inhomogeneity, as illustrated at 2 to 3μ. In order to dehydrate the specimen, it was necessary to dismount the section from its cardboard support and place it in a porcelain tube which was then heated with a bunsen flame or blast lamp. The specimen was weighed before and after heating, and knowing the water content before heating it was possible to compute from the loss in weight the water remaining after heating. For example: Starting with the section weighing 32.037 mg the loss in weight was 0.360 mg. The original water content was 3.6 per cent, from which it was computed that for curve *b*, figure 6, the water content was 2.5 per cent. The weighings were made by Mr. W. C. Bishop, whose long experience in such work insured both speed and high accuracy. The weighings were made on an assay balance taking a maximum load of 1 gram. The working sensitivity was 1 mg = 10 divisions; probable error of a single weighing 0.002 to 0.005 mg. It was found that the weighings became constant in less than 10 minutes after dehydration. It will be shown presently that this specimen absorbed about 0.06 per cent of water per day. Since the weighings were completed and the specimen was remounted within 15 minutes after dehydration, and since the observations on the absorption band at 3μ were completed within 45 minutes after heating the specimen, this question of reabsorption (so frequently asked by all comers) needs no further consideration. Curves *c*, *d*, and *e* were obtained in the same manner as curve *b*. Each time the section was dismounted there was a slight loss due to breakage, so that after obtaining curve *e* the specimen was placed

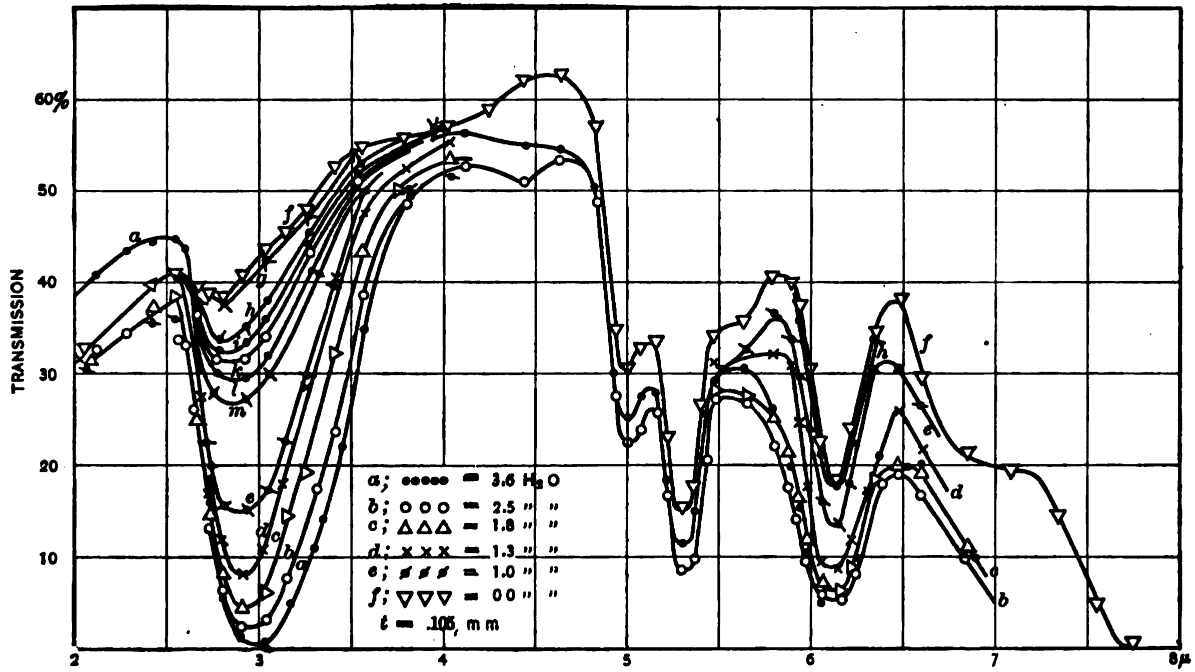

Fig. 6.—*Opal,* SiO_2+xH_2O. *Showing the Variations in Transmissions Before (Curve a) and After (Curves b to f) Successive Dehydrations; also After Successive Rehydrations (Curves g to m). a=3.6 Per Cent Water; b=2.5 Per Cent Water, etc.*

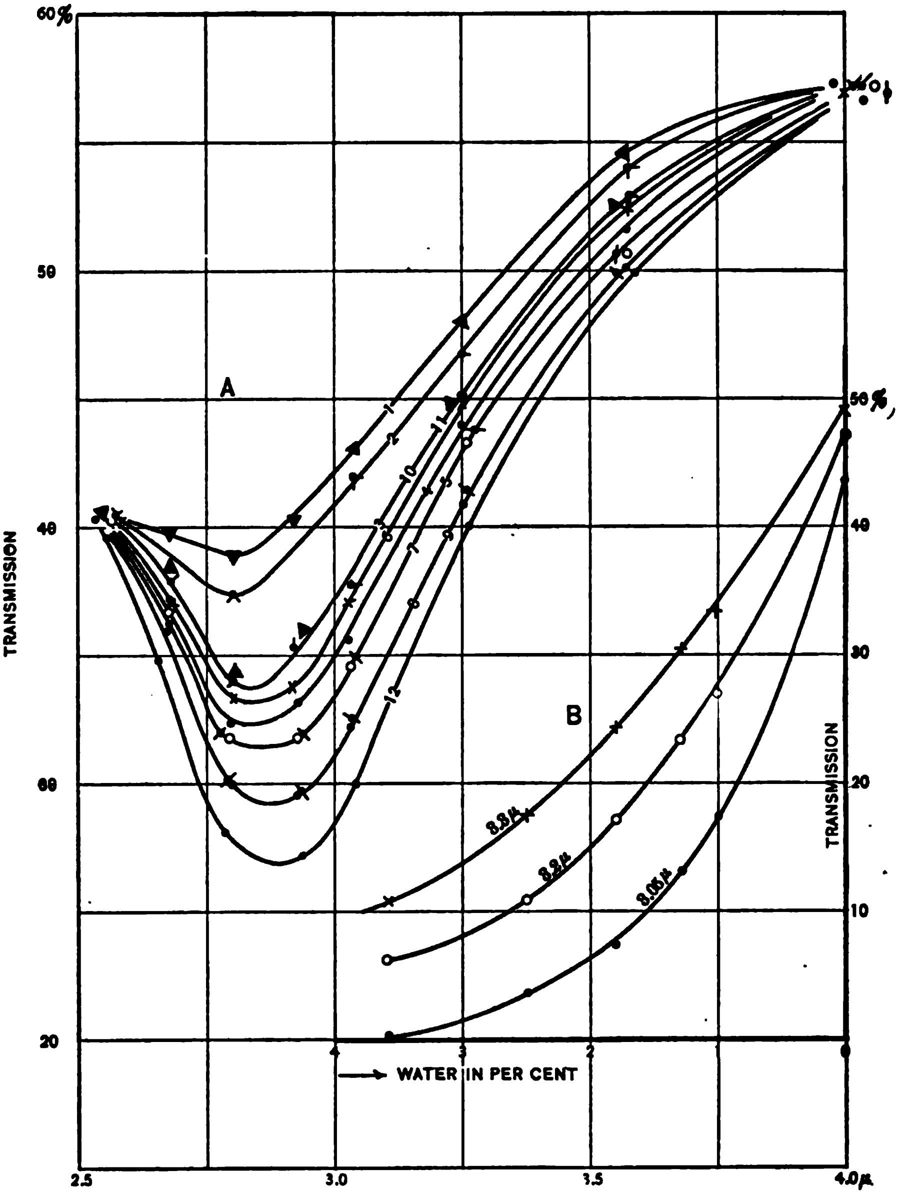

Fig. 7.—*Showing the Variation in the Water Content of Opals on Successive Days After Dehydration*

in a platinum receptacle and heated to a bright red (700°) for one hour. It was then mounted permanently upon the cardboard support and on examination gave curve *f*, figure 6. The small band at 2.9μ remains; but whether it is due entirely to SiO_2 or whether it still represents a trace of water remains undetermined. After standing overnight it reabsorbed moisture, giving curve *g*. Two days thereafter the transmission had fallen to curve *h*. This examination of the reabsorption of water was continued for 17 days after dehydration, the relative humidity of the laboratory being determined daily by means of an aspiration hygrometer. The daily variation of the absorption band at 3μ is shown in figure 7–A, which represents curves *f*, *g*, . . . *m*, figure 6, on a different scale. The numbers attached to the various curves indicate the order in which they were observed. In figure 7–B are given several isochromatic transmission curves, obtained from curves *a*, *b*, *c*, *d*, and *e* of figure 6. From these curves it is possible to obtain a rough estimate of the water content represented in the curves 2 to 12, figure 7–A. The disappearance of the water band at 6.1μ is not so marked as at 3μ, but it is evident that in making allowance for variation in homegeneity this part of the curves can not be superposed. The bands at 5.0μ and 5.3μ are due entirely to silica and there would be no difficulty in superposing them. It will of course be understood that in the frequent remounting of this specimen it was not possible to obtain the transmission of exactly the same part of the section each time.

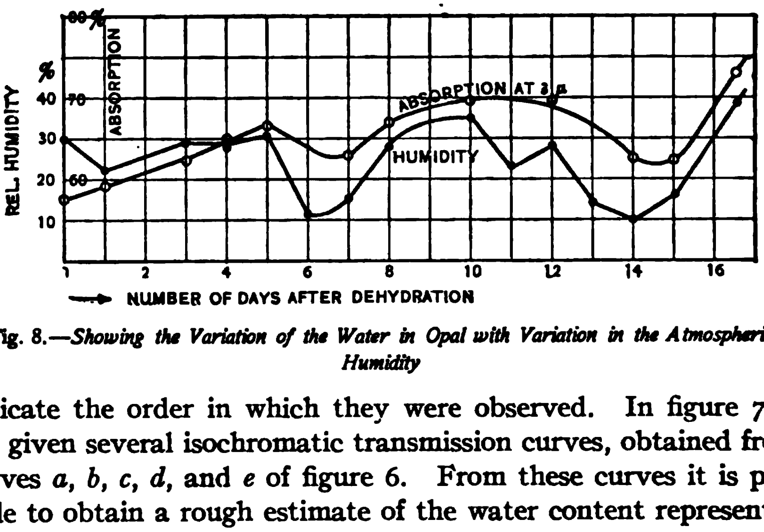

Fig. 8.—*Showing the Variation of the Water in Opal with Variation in the Atmospheric Humidity*

During the examination of the rehydration of this sample of opal there were two cold periods when the relative humidity decreased to 10 per cent. It was then found that the opal became dehydrated. This is illustrated in figure 8, which shows the variation of water in opal (as measured by the variation in the absorption) with variation of atmospheric humidity. There is a lag of about half a day in the hydration curve.

GROUP 2. MINERALS CONTAINING WATER OF CONSTITUTION

Under this heading are collected the minerals which contain water, but which do not show the characteristic absorption bands found in water in its free liquid state.

Muscovite Mica, $H_2KAl_3(SiO_4)_3$.—The transmission spectra are given in figure 9. Curve *a* was obtained with a rock salt prism, while curves *b* and *c* were observed with a fluorite prism. The thickness was 0.04 mm. Curve *b* shows the transmission of the specimen after dehydration. The absorption bands are common to silicates; and none are in common with those of water. The band of selective reflection beyond 9μ does not seem to be affected by the constitutional water, as should be the case, since it is known that these bands are due to the SiO_2 radical. The other bands disappear on dehydration. The layer of mica is too thin, and the inhomogeneity is too great to show the weak absorption band of silica at 2.9μ. A more complete list of minerals containing water of constitution is given in previous communications[17] on this subject.

Tremolite, $CaMg\ (SiO_3)_4$.—The transmission of a section of this mineral, 0.23 mm in thickness, was described in a previous paper.[18] The section was kindly prepared by Dr. Allen, of the Geophysical Laboratory, who found 2 per cent of water, which appears to be present in solid solution. The section of tremolite was of sufficient thickness to insure detecting the water, provided its absorption is as great as in the liquid phase. The equivalent layer of water was 0.0138 mm, but no water bands could be detected. It is evident from this and from the transmission of a layer of water 0.014 mm in thickness (Fig. 1, *b*), that the water in tremolite is in an entirely different condition from that which obtains in the crystals and in the solid solutions previously investigated by this method of analysis. Thinking that further information would be disclosed, the investigation of this interesting mineral was undertaken anew, using samples of the same specimen previously examined.

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[17] This Bulletin, **2**, p. 457; 1907. Carnegie Publication No. 65.

[18] Physical Review, **30**, p. 326; 1910.

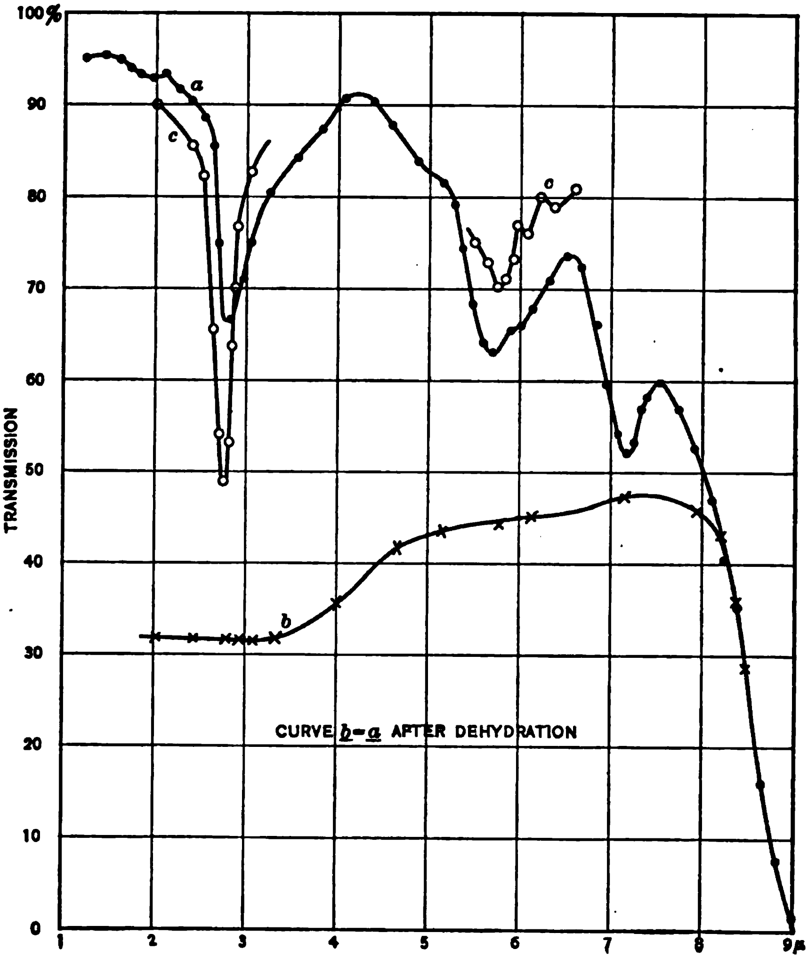

Fig. 9.—*Muscovite Mica*, $H_2KAl_3(SiO_4)_3$

In the earlier work[19] it was found that a sample of amphibole (probably hornblende) showed no traces of water, the small absorption band at 2.9μ being similar to that found in feldspars.

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[19] Carnegie Publication No. 65, p. 64.

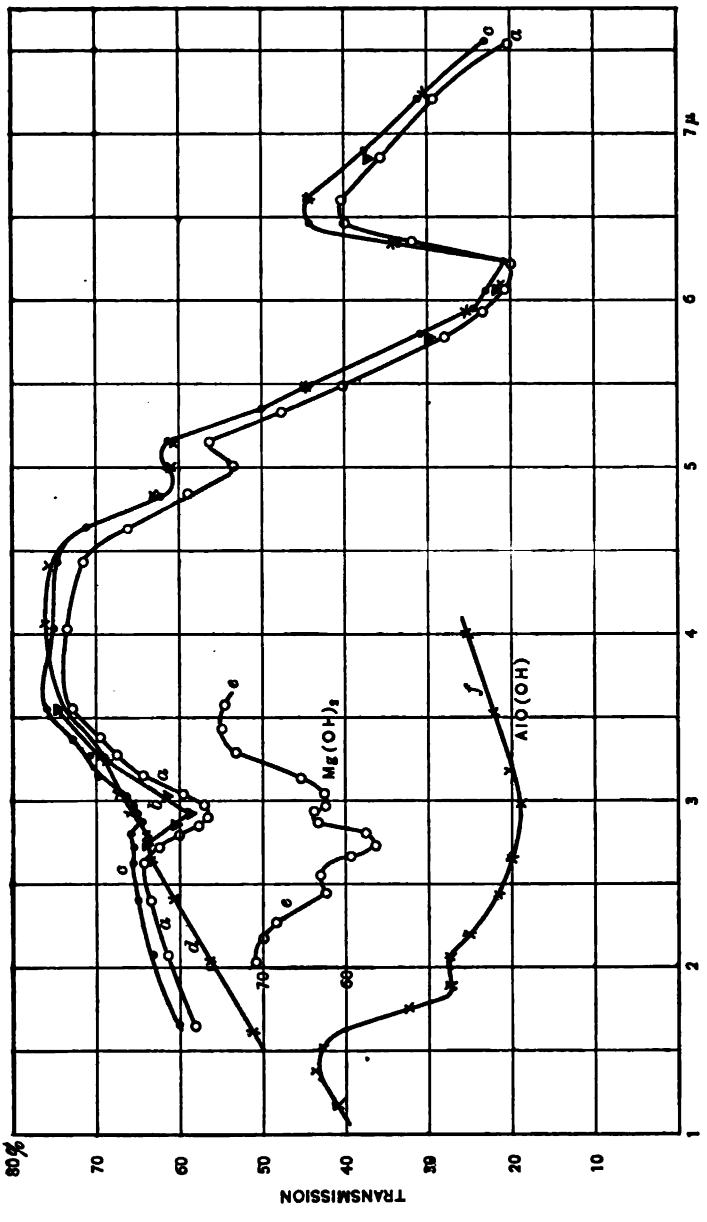

Fig. 10.—*Tremolite, CaMg* $(SiO_3)_4$

The sample of tremolite used in the present examination was 0.095 mm in thickness. The small absorption bands at 2.9 and 6.2μ are, therefore, not so sharp as found in the 0.23 mm sample previously examined. On the assumption that 2 per cent of water was present, the equivalent layer of water (sp. gr. of tremolite is 3) is 0.0057 mm in thickness.

The transmission of this sample before dehydration is given in curve *a*, figure 10. Curve *b* represents the transmission after heating the specimen for half an hour at 200° in an atmosphere of dry hydrogen. The curve is superposable upon curve *a*. Curve *c* gives the transmission after heating the specimen in an electrically heated porcelain tube furnace at 500° for five hours. In this case the absorption band at 2.9μ is practically destroyed. Curve *d* gives the transmission after heating the specimen in the electric furnace at 925° for five hours. The absorption is identical with that of curve *c*, showing that most of the chemical change was brought about at 500°. In the dehydration the specimen became slightly inhomogeneous, which caused a scattering of the radiation to 3μ. The band at 2.9μ has entirely disappeared, showing that it belonged to the compound that existed before dehydration. The bands at 5 and 6μ have undergone no change. They belong to anhydrous silicates; and the general outline of the transmission curve is not unlike that of the feldspars.[19]

In figure 10 are also given the transmission curves of brucite, $Mg(OH)_2$, and of diaspore, $AlO(OH)$. The brucite curve shows a complex region of absorption bands at 2.5, 2.75, and 3.0μ. The 3μ band is found in substances having OH groups. In diaspore the absorption is very complex and the individual bands, which no doubt exist, are not resolved. Bauxite, $Al_2O(OH)_4$ and göthite, $FeO(OH)$, also have wide bands at 3μ.

The chemical composition of amphiboles, of which tremolite is a species, does not appear to be definitely known, some[20] arriving at the conclusion that the water is present as "dissolved water," while others[21] considered the water to be present as hydroxyl groups combined with Al_2O_3 and Fe_2O_3. From the present data it is evident that the water in tremolite is not present in the same condition as in other substances containing water in solid solution or dissolved water. Attention has already been called to the fact that in selenite the density of water is much less than in the free state, so that a layer of water equivalent to 0.31 mm transmits radiation to 6μ, while a film of water 0.31 mm in thickness is completely opaque beyond 2.5μ. The "density" of water in opal is far less than in selenite, but its opacity is of the same order of magnitude. Again, if we consider opal, having 3 per cent of water (sp. gr. $=2$), we find that 6 per cent of the thickness of the section is water and the absorption bands of water are very prominent, while in tremolite (sp. gr. 3), in which the thickness of the water layer is also 6 per cent, the absorption bands of water are entirely lacking.

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[19] Carnegie Publication No. 65, p. 64.

[20] Allen and Clement: Amer. Jour. Sci., **26**, p. 101; 1908.

[21] Penfield and Stanley: Amer. Jour. Sci., **23**, p. 23; 1907.

From the present data it appears that in tremolite the water is constitutional, with OH groups, the small band at 2.95μ being complex, as in the other hydroxides just cited. This is, of course, contrary to the vapor pressure experiments; but it is the most satisfactory conclusion to be drawn from the present experiments.

GROUP 3.—MISCELLANEOUS SUBSTANCES

Under this heading are described the absorption or reflection spectra of several substances having no direct bearing on the present problem. They are, of course, only supplementary to previous work to which reference must be made in order to gain an intelligent understanding of their spectral characteristics.

Gelatin.—This substance belongs to the albumens, of which the chemical constitution is unknown. They contain C, H, O, N, and S. The present examination was made to determine the variation in intensity of the water bands with variation in the water content. The sample examined was a sheet of commercial material 0.025 mm in thickness, and it was perfectly clear. Curve *a*, figure 11, gives the transmission curve before dehydration, and curve *b* gives the transmission after partial dehydration, the film being tinged a faint light brown. The peculiarity of these curves is the absence of absorption bands at 1.5 and 2μ. The general appearance of the transmission curve is entirely unlike that of water, and of substances containing water. The absorption bands are sharp and narrow, as usually found in carbohydrates. In fact, the whole curve appears as though the water were present as "water of constitution," the sharp band at 3μ being due to OH groups. The 3.4 and 6.8 and 7.3μ bands are characteristic of substances rich in CH_2 and CH_3 groups. The very sharply bounded region of great opacity at 6 to 8μ is characteristic of carbohydrates containing NO_2 groups. There are absorption bands at 2.4, 3.0, 3.43, 4.0, 4.6, 4.9, 5.15, 5.5, 6.0, 6.8, 7.3, and 8.1μ.

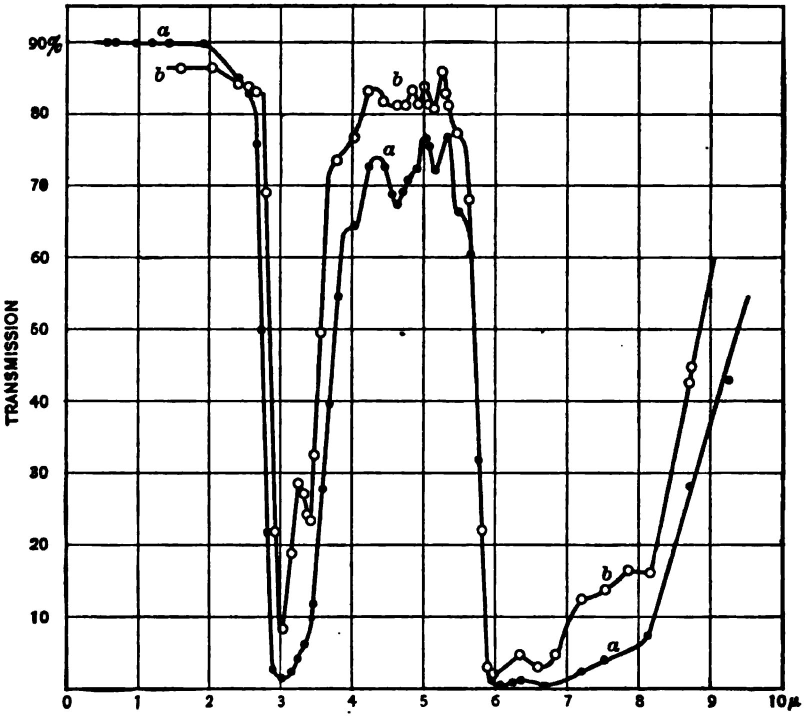

Fig. 11.—*Gelatin* (*Curve b After Dehydration*)

Oleic acid, $C_{17}H_{33}COOH$.—This substance was examined to obtain a check on previous work done with a rock-salt prism and to arrive at an explanation of the peculiar absorption bands found in olive oil and in linseed oil. In all cases the film of oil or acid was contained between clear fluorite plates, separated by a ring of tinfoil 0.007 mm in thickness, curve *c*, figure 12.

The paraffin oils have a series of harmonic bands at 1.71, 3.43, 6.86, (7.35), and 14μ. In the fatty acids the region of 3.5μ and 7μ is complex and a large absorption band is found at 5.8 to 5.9μ.

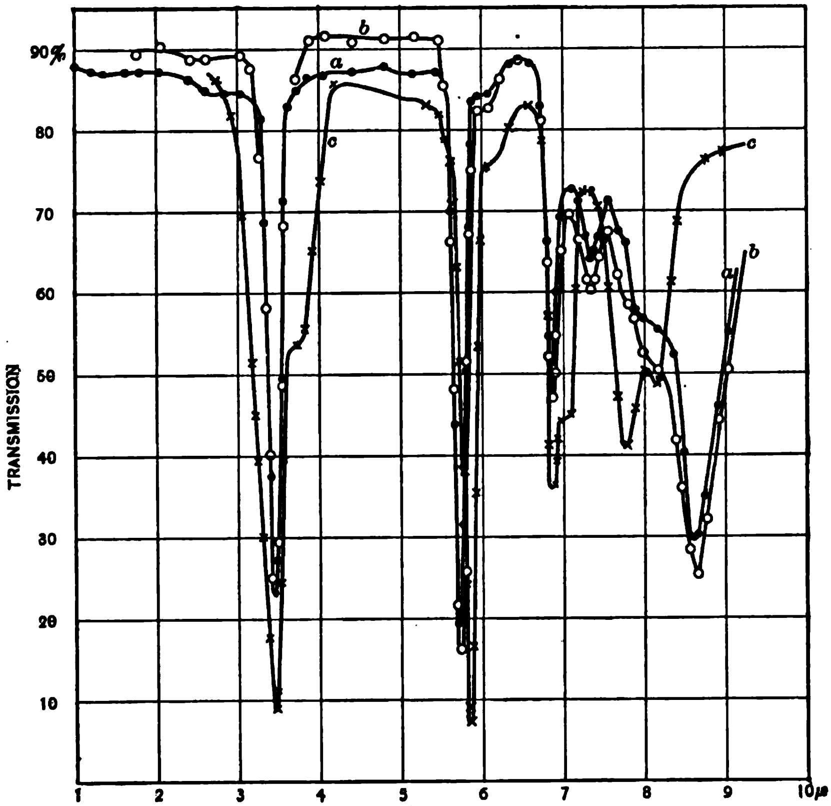

Fig. 12.—*Olive Oil* (*a*); *Linseed Oil* (*b*); *Oleic Acid* (*c*). *Thickness*=.*007 mm*

The latter band was sometimes found in some of the heavier paraffin oils when the absorption cell was exposed to oxidation.[22]

In previous investigations the intense band at 5.8μ was found in all substances containing the C = O group, as in COOH. It was also found that in passing from a saturated fatty acid (stearic acid, $C_{17}H_{35}COOH$) to an unsaturated fatty acid (oleic acid, $C_{17}H_{33}COOH$) there is no marked change in the absorption spectrum. The most noticeable feature, as the number of CH_2 and CH_3 groups increases, is the disappearance of small bands at 3.8 and 7.08μ, and an increase in sharpness of the 3.43, 6.86, 7.35, and 8.65μ bands which are characteristic of the paraffin oils. In other words, as the ratio of the total number of CH_2 and CH_3 groups to the COOH groups increases (c. f. acetic acid, CH_3COOH, and stearic acid, $C_{17}H_{35}COOH$) the characteristic absorption bands of the CH_2 and CH_3 groups become more prominent with the disappearance of the bands characteristic of the COOH groups. The work is also instructive in showing that not until we can use a very much larger dispersion than is now employed can we expect to obtain much information from the study of complex absorption bands, such as are found in the fatty acids. As indicated elsewhere,[19] a detailed study of individual groups of compounds is highly desirable, now that a preliminary survey of the various groups of compounds has been made. It seems quite probable that by using a very much larger dispersion than has been employed heretofore, some of the older data will not be verified, but will be found to be mere hints to much more useful information. It is to be noticed that the fluorite prism resolves the band at 3.43 and 3.8μ, which was not possible in the previous investigation with the rock-salt prism. The maxima of the absorption bands of oleic acid occur at 3.43, 3.8, 5.86, 6.1, 6.86, 7.08, 7.75, and 8.15μ. The sample examined was a highly purified one from Merck.

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[22] See Figs. 64, 72, and 73, Publication No. 35, Carnegie Institution of Washington, 1905.

Olive oil.—The transmission curve of this substance is shown in curve *a*, figure 12; (thickness of film = 0.007 mm). The curve is conspicuous for the sharpness of the absorption bands at 3.43 and 5.7μ. This oil is a mixture of various fatty acids. The 3.8 and 7.08μ bands are absent. There are absorption bands at 2.7, 3.43, 5.7, 6.1, 6.86, 7.35, 7.75, 8.15, and 8.65μ. The 5.7μ (shifts to 5.9 in some compounds) is characteristic of substances containing CO groups.

Linseed oil.—This oil consists entirely of unsaturated acids, including oleic acid (one double bond) and linolenic acid, $C_{17}H_{29}COOH$ (three double bonds). The absorption band at 5.7μ, curve *b*, figure 12, is shifted from that of the preceding (more saturated) oil, being at 5.75μ, while in the pure unsaturated acid, oleic acid, the band occurs at 5.85μ. No explanation is at hand for the occurrence of the band at 8.65μ, which is found in the paraffin oils but does not occur in any of the fatty acids. The sample examined was a standard test sample, free from adulterants. The maxima of the prominent absorption bands occur at 3.43, 5.75, 6.1, 6.86, 7.35, 7.75, 8.15, and 8.65μ.

Chitin.—This is a complex nitrogenous substance the chemical structure of which is unknown. The samples examined were the outer, horny, amorphous integument covering various species of fireflies, the color varying from white (covering of the luminous organs) to a deep brown. The examination was made in connection with the question [23] whether or not an appreciable amount of energy, of wave lengths greater than 2 to 2.5μ could be transmitted (radiated) through the body of the insect, assuming that such energy is generated in the photogenic cells. In figure 13, curve *a* gives the transmission through one of the horny abdominal segments of a dried specimen of the "Cuban firefly," Pyrophorus noctilucus. This integument is dark brown (in reflected light) which causes a heavy absorption through the visible spectrum to the red, at which point the transmission rapidly increases. In

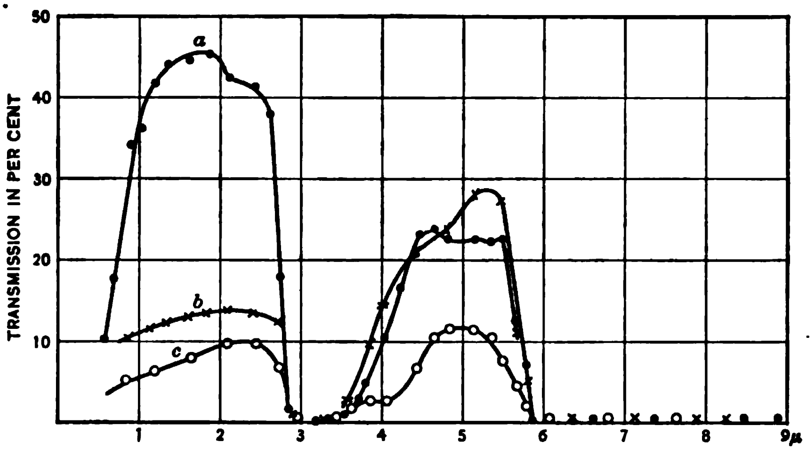

Fig. 13.—*Chitin* (*the Chitinous Layer of Fireflies*)

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[23] Ives and Coblentz: This Bulletin, 6, p. 321; 1909. Coblentz: Electrical World, 56, p. 1012; 1910.

this firefly, it may be recalled, the abdominal light is emitted through a slit between two of the segments of which the above is a sample. The size of the specimen examined was about 1.5 by 7 mm. In this same illustration, figure 13, curve *b* gives the transmission through one of the eyelike fenestrate membranes on the thorax of the "Cuban firefly," and through which is emitted the so-called "thoracic light." The specimen was only 1.5 by 2 mm and hence very difficult to examine. After removing all the photogenic cell ligaments which adhered to it this specimen was fairly translucent. In the region from 1 to 2μ the transmissivity is probably higher than observed, the low values being due to scattering of the radiation in passing through the specimen.

Curve *c*, figure 13, gives the transmission through the outer integument covering the photogenic cells of Photinus pyralis. The specimen examined was a single dried abdominal segment, 1.5 by 4 mm, which had been moistened in water and freed from all ligaments and photogenic material. The specimen was not very smooth and it was only semitranslucent. No doubt a better sample could have been prepared by dissecting a fresh undried insect. In both curves *b* and *c* the opacity at 1μ to 2μ and at 5μ is greatly increased by scattering of the transmitted radiation which did not reach the bolometer. However, as was anticipated in a previous communication, these curves have the characteristic absorption spectrum of complex carbohydrates, in which there is great (and usually complete) opacity from 2.8μ to 3.8μ, and beyond 6μ, with a fairly transparent region at 4.5μ to 5μ.

It may be noticed that these specimens were dry. If they had been fresh then the water would have absorbed most of the radiation at 4 to 5μ.

The data show that but little radiant energy (if generated in the photogenic cells) of wave-lengths greater than 2.5μ will get out of the insect's body. That which does get out, at 4 to 5μ, will be so weak in intensity that it will hardly be distinguishable from the emission spectrum of the "animal heat" which has its maximum emission in the region of 7μ.

Sylvite, KCl.—The fact that sylvite has absorption bands in the region of 3μ and 7μ was mentioned by Rubens [24] but no further reference being made thereto by other writers the question arose [25] whether this is a common property of this mineral or whether the bands described by Rubens were due to impurities. The present examination was undertaken as a result of inquiries sent to this bureau as to the suitability of sylvite for radiometer [26] windows, and as to its freedom from absorption bands.

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[24] Rubens: Ann. der Phys., **58**, p. 267; 1894.

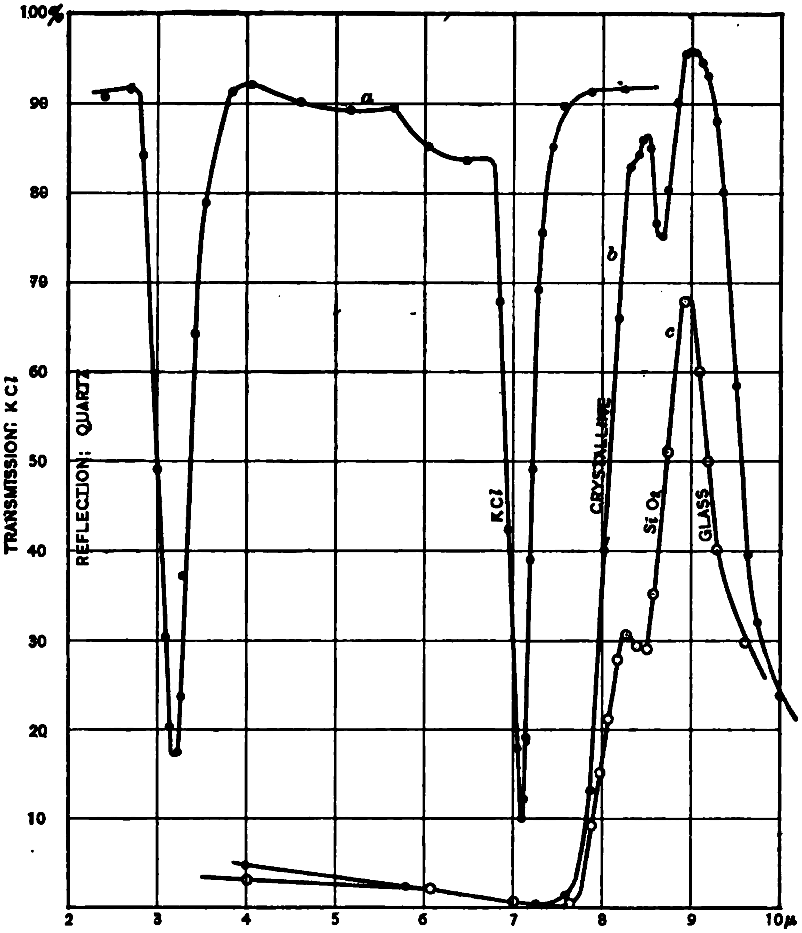

Fig. 14.—*Sylvite, KCl. Quartz, SiO$_2$; Crystalline b and Amorphous c*

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[25] Kayser: Spectroscopie, vol. 3, p. 387.

[26] It seems desirable to employ the term "radiometer" instead of the more clumsy expression "radiationmeter" when the general instrument is mentioned, using the term "bolometer," "thermopile," "radiomicrometer," "radiobalance," "Nichols radiometer," etc., when the reference is to the specific instrument.

The transmission of sylvite curve *a*, figure 14 (thickness = 4 mm) shows two very sharp absorption bands, at 3.18μ and 7.08μ, respectively, and a smaller depression at 6.2μ. An interesting point in connection with these absorption bands is their assymmetry, indicating that they are double, just as was found true of the bands of residual rays [27] at 62 to 70.3μ.

The thickness of the plate of sylvite was 4 mm. A very much thicker plate should be used to investigate the assymmetry at 3.6μ and 7.3μ.

Quartz, SiO_2.—The reflecting power of a plate of crystalline quartz is given in curve *b*, figure 14. It was observed several years ago with a rock-salt prism, but never published because of the doubt as to the accuracy of the indications of the appearance of a double band at 8.3μ and 8.5μ, and the assymmetry at 9μ and 9.2μ. Recent investigations [28] using a very much larger dispersion shows that these bands are complex.

Quartz glass.—The present sample of quartz glass was examined several years ago and described in Carnegie Publication No. 97, page 22. The examination was made entirely separate from all the rest of that work, using a special adjustment of apparatus, which may account for the inconsistent results obtained, which showed an entirely different spectrum from that of crystalline quartz. There being no good reason why crystalline and amorphous quartz should give entirely different spectra at 7.8μ the work was repeated on the same sample previously examined, using a vacuum bolometer which was far steadier than the old-style instrument previously employed.

In the present examination the rear surface of the quartz-glass plate was painted black to avoid stray light. The results are shown in curve *c*, figure 14. The first maximum at 8.3μ reflects 31 per cent, while the second maximum, at 8.95μ, reflects 68 per cent. The band previously found at 7.8μ is entirely lacking, and the reflecting power throughout this whole region is too small to be measured, whereas in the previous examination the reflecting power was high, about 5 per cent. Up to the present time no explanation can be offered for the presence of the spurious band previously observed at 7.8μ. The other reflection bands are practically the same as previously observed, and the whole spectrum appears much simpler than that of crystalline quartz. In the work recently described by Reinkober[28] the positions and the intensities of the maxima of quartz glass are almost identical with the present results.

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[27] Rubens and Hollnagel: Sitzber. Akad. Wiss. Berlin, p. 26: 1910. Hollnagel. Inaug. Dissertation, Berlin, 1910.

[28] Trowbridge and Wood: Phil. Mag., **20**, p. 898; 1910. Reinkober, Ann. der Phys., **34**, p. 343; 1911.

VIII. LIGHT FILTERS WHICH ABSORB ALL THE INFRA-RED

There are numerous problems in which it is desirable to separate the infra-red from the visible spectrum without employing a prism. The use of absorption screens is the most natural procedure, provided suitable material can be found. Water is the most opaque substance known, a layer 1 cm in thickness absorbing all wave lengths greater than 1.4μ. Substances which are perfectly transparent in the visible spectrum, and which have large absorption bands just beyond the visible, between 0.8 and 1.5μ, are unknown. The nearest approach to the fulfillment of such a condition is the mineral beryl[29] which in polarized light (the ordinary ray) has a large absorption extending from 0.7μ to 1μ with a maximum at 0.86μ.

Numerous searches have been made to find a substance which in solution with water absorbs all the radiation lying between 0.7μ and 1.4μ. The old idea that a solution of potassium alum absorbs more of the infra-red than pure water has been repeatedly proven erroneous. Of late, experimenters[30] have been using solutions of ammonium-iron alum $[(NH_4)_2Fe_2(SO_4)_7]$ claiming that it was more opaque than pure water. This is due to the fact that the solution is not entirely colorless. This is illustrated in figure 15, curve *a*, which gives the transmission of a saturated (at 25°) solution of this substance. The transparency gradually increases, so that at 1.2μ the absorption is but little greater than same thickness of pure water. It is therefore evident that in experiments where an attempt is made to eliminate the infra-red from the visible radiation, e. g., in incandescent lamps, it is brought about with a great loss of light with but little gain in the attempt to eliminate the infra-red.

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[29] Koenigsberger: Ann. der Phys., 61, p. 687; 1897.

In measuring the luminous efficiencies of light sources Féry[31] and others have separated the visible from the total radiation by means of solutions of copper salts, e. g., copper acetate of such concentration that the minimum of the absorption band was at 0.54μ. The transmission curves of these salts coincide closely with the sensibility curve of the eye.

An efficient screen, either colored glasses or solutions of salts, permits the use of a surface bolometer, which is much better adapted than the linear bolometer for measuring radiation which is of low intensity. For example, the mercury arc consists of strong lines in the green and the blue and a series of strong emission bands in the region of 0.9 to 1.3μ. The water cell will not absorb this infra-red radiation, but, as will be shown presently, a weak solution of copper chloride will absorb it without serious loss of energy in the visible spectrum. Hence, the employment of a surface bolometer and an absorption cell of copper chloride, even if it does absorb some of the visible, will be far more efficient than the use of a linear bolometer. The latter requires a spectrometer, through the slit of which it is possible to pass only a small part of the light which can be used on a large surface bolometer.

It was therefore of interest to examine a series of solutions, which seemed promising as absorption screens, to determine the least concentration which would absorb all the infra-red radiation, and at the same time absorb but little in the green and the blue.

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[30] Lux: Zs. für Beleuchtungswesen, Heft., **16**, p. 36; 1907. Russner: Phys. Zs., **8**, p. 120; 1907.

[31] Féry: Bull. Soc. Franc. de Physique, p. 148; 1908. Bull. Soc. Internat. des Électriciens, **9**, p. 655; 1909.

The transmission curves of a series of colored glasses were described elsewhere.[32]

For the present experiments a Nernst glower was used as a source of radiation. It was placed at a distance of about 10 cm from the spectrometer slit in front of which stood the glass absorption cell. This great distance reduces the radiation considerably, so that no high accuracy can be claimed for the measurements in the violet. Furthermore, the visible spectrum is too narrow (a fluorite prism was used), so that for quantitative work of the highest precision the absorption in the visible will have to be determined anew, using a larger dispersion. For this region of the spectrum the spectrophotometer would be better than the linear bolometer. The glass absorption cell was 2.1 cm in thickness, the glass walls being 2 mm in thickness. The saturated solutions mentioned in this paper were made at 25° C.

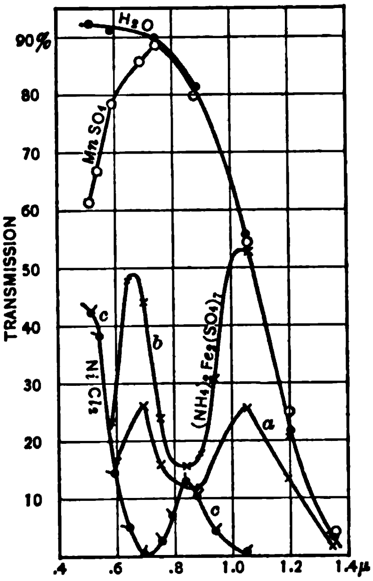

Fig. 15.—*Water; Manganous Sulphate; Nickel Chloride; Ammonium-Iron Alum*

Manganous sulphate, $MnSO_4$.—The transmission curve (. . .) of a saturated solution of manganous sulphate is given in figure 15. Beyond 0.8μ the transmission coincides with that of the same thickness of pure water. *Potassium dichromate*. $K_2C_rO_7$, absorbs the violet and is transparent in the infra-red.

Ammonium-iron alum, $(NH_4)_2Fe_2(SO_4)_7$.—In figure 15, curve *a* gives the transmission of a saturated solution (slightly acid), and curve *b* gives the transmission of a highly concentrated solution of ammonium-iron alum. There is a large absorption band at 0.85μ. Beyond 1μ the transmission of the concentrated solution is as high as that of the same thickness of pure water. The transmission curve of ammonium-iron alum published by Nichols[22] does not show the band at 0.85μ.

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[32] Publication No. 97, Carnegie Institution of Washington; 1908.

Nickel chloride, $NiCl_2$.—The saturated solution transmitted but little radiation. The solution was therefore diluted to three times its volume. The transmission of the latter solution is given in curve *c*, figure 15. The transmission is less than 50 per cent in the green, while at 0.85μ there is an appreciable transmission amounting to 13 per cent at the maximum.

Nickel nitrate was also examined, and a similar (high) transmission band was found at 0.85μ. It therefore appears that these nickel salts are not suitable for absorption screens.

Copper sulphate, $CuSO_4+5H_2O$.—The transmission curve (. . .) of a saturated solution of copper sulphate is given in curve *d*, figure 16. There is complete opacity beyond 0.6μ. The transmission is high in the blue, so that this substance is suitable for eliminating all but the blue light.

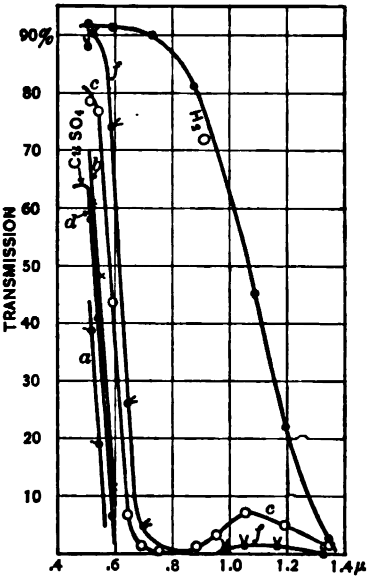

Fig. 16.—*Copper; Acetate* (*a, b, c*), *Sulphate* (*d*), *and Potassium Chloride* (*f*)

Copper potassium chloride, $CuCl_2\text{-}2KCl+2H_2O$.—The transmission of a 2.5 per cent solution of copper potassium chloride is given in curve *f*, figure 16. Its transmission is not much greater than cupric chloride in the visible while at 1.1μ it transmits 1.2 per cent against 0.67 per cent for the same concentration of cupric chloride. See figure 17.

Copper acetate, $Cu(C_2H_3O_2)_2$.—The transmission of a 5 per cent (2 g in 38 cc H_2O, 3 drops acetic acid) solution of copper acetate is given in curve *a*, figure 16. Curve *b* gives the transmission of a 2.5 per cent solution and curve *c* gives the transmission of a 1 per cent solution of copper acetate. The latter transmits too much infra-red radiation (about 7 per cent at 1.05μ) to be of great use as an absorption screen.

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[22] E. F. Nichols: Phys. Rev., 1, p. 1; 1896. See also Carnegie Publication No. 97, p. 50; 1908.

Cupric chloride, $CuCl_2+2H_2O$.—The most suitable screen for absorbing the infra-red, and at the same time having a high transmission in the yellowish green and in the blue is cupric chloride. This is illustrated in the various curves given in figure 17. Curve *1* gives the transmission of a 10 per cent solution (2 gr. $CuCl_2$ + 18 cc H_2O + 2 drops of 20 per cent HCl) of cupric chloride. Curve *2* gives the transmission of a 10 per cent solution containing 0.5 cc of 20 per cent HCl. This shows that the addition of acid has no effect on the infra-red, and but little effect in the visible. Curve *3* gives the transmission of a 5 per cent solution; curve *4* a 2.5 per cent solution, and curve *5* a 1 per cent solution. The latter transmits a very considerable amount of infra-red radiation, hence unsuitable as a screen. The 2.5 per cent solution, curve *4*, transmits 0.0067 at 1.1μ (in the dotted curve *4* at 1.1μ the ordinates are multiplied by 20) which is negligible. A further examination was made of a very accurately prepared 2 per cent solution. It transmitted 88 per cent at 0.54μ, 67 per cent at 0.589μ, 20 per cent at 0.646μ, and 0.69 per cent at 1.1μ. It may therefore be assumed that a 2-cm layer of a 2 per cent solution (2 g $CuCl_2$ in 98 cc H_2O) of cupric chloride absorbs all the infra-red beyond 0.67μ and transmits from 80 to 85 per cent at 0.5μ and about 70 per cent at 0.58μ, which is in the region of the yellow mercury line.

In separating the yellow from the green or blue lines it is, of course, necessary to combine the absorption cell of cupric chloride with a monochromatic red, green, or blue (for the blue, the copper sulphate solution may be sufficient) glass. This, of course, reduces the intensity still further, but it will hardly fall below 50 per cent of its original value. When we consider that the sensitivity of a bolometer is closely proportional to the square root of the surface and that a linear bolometer is never larger than 1 by 15 mm (usually 0.5×10 mm), while a surface bolo-

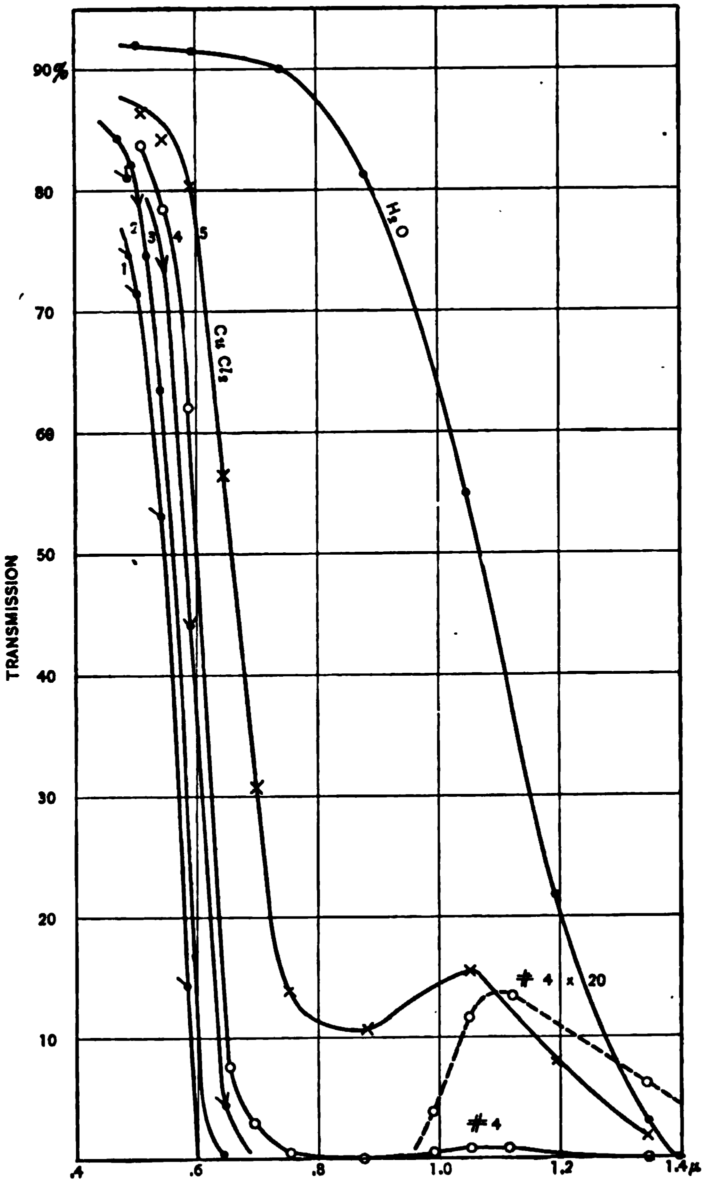

Fig. 17.—*Cupric Chloride*, $CuCl_2+2H_2O$

meter is at least 40×50 mm, the advantage of the latter combined with an absorption cell is apparent. Take, for example, the determination of the mechanical equivalent of light, in connection with which the present question of absorption screens was undertaken. The determination of the mechanical equivalent of light requires an accurate measurement of the candlepower of the light used and its value in energy units. The determination of the candlepower is an easy matter. The determination of the energy equivalent is beset with such difficulties that measurements made with the best instruments (absolute bolometers and calorimeters) for measuring radiation in absolute units differ by 5 to 10 per cent. Until some of these radiometric difficulties have been overcome it is, of course, futile to discuss the various proposals of a unit of light based upon its energy equivalent in absolute measure.

IX. SPECTRAL LINES SUITABLE FOR INFRA-RED REFERENCE STANDARDS

If the optical constants of the material used are unknown it is usually more convenient to calibrate a prism (or a wire grating) by picking out sharply defined emission or absorption bands, such as those noticed in sylvite on a previous page. The accuracy attainable in determining the position of the maximum of such a reference standard is of the order of 0.02μ, depending upon the experience of the observer.

It is beyond the scope of the present note to discuss the various instruments, and the most suitable prisms and standard lines to be used in spectroradiometry, that part being left for some future time. Reference standards must be easily obtainable, otherwise it is quicker to compute the calibration curve from the refractive indices and the angle of the prism. In his experiments on residual rays, lying between 8μ and 60μ, the writer calibrated [34] his wire gratings by means of the residual rays reflected from quartz fluorite, mica, and rock salt.

As a fiducial line the writer uses the yellow helium line, $\lambda=$ 0.5876μ, as obtained in an ordinary vacuum tube, and any other point in the infra-red is read from the spectrometer circle. For example, the sharp absorption band of sylvite at 3.18μ, usinga 60° fluorite prism, is found at a distance of 1° 25′ from the yellow helium line.

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[34] Carnegie Publication No. 65, p. 25, 1908.

The standard lines may be produced by emission of incandescent solids and gases; by transmission through solids, liquids, or gases; and by reflection from plane, highly polished surfaces of solids or the surface of a liquid.

The radiation from an ordinary Bunsen burner furnishes an intense, sharply defined emission band at 4.40μ.

Sharp bands of selective emission of oxides in the form of solid rods, heated electrically or in the form of powders upon a heater, are easily produced.[35]

Zirconium oxide with very sharp maxima at 2.83μ and 4.3μ, feldspar with sharp maxima at 2.88μ and 4.5μ, and talc with a group of maxima at 2.42μ, 2.75μ, and 3.35μ, respectively, are excellent standards of this type. Salts of various metals in the arc of cored carbon electrodes give strong emission bands[36] near the visible spectrum. This type of radiator is not easily operated. The mercury arc is better adapted, and it has strong maxima at 1.014μ and 1.129μ, respectively. Helium gas (vacuum tube) has maxima at 1.08μ and 2.06μ, observable with delicate instruments.

Transmission spectra are the most easily observed, as noticed on a previous page, and the number of absorption bands suitable reference standards is too numerous to mention. Without elaborate accessory apparatus a rock-salt or a fluorite prism can be calibrated by resorting entirely to transmission spectra. For example, a film of water between fluorite plates, or a plate of selenite, gives the bands at 1.5, 2, 3, 4.75, and 6.08μ. A film of collodium has sharp bands at 6.05μ and 7.85μ. A better example[37] and one that would cause less confusion is potassium dichromate with a single, very intense absorption maximum at 5.4μ, or potassium chlorate which has a similar maximum at 5.25μ. Sylvite has a pair of very sharp absorption bands at 3.18μ and 7.08μ, respectively. Oleic acid has strong absorption bands at 5.86μ,

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[35] This bulletin, 5, p. 159; 6, p. 301, 1910.

[36] See Carnegie Publication 35, 1905. This bulletin, 2, p. 457, 1907.

[37] Carnegie Publication 65, p. 57, 1908.

10.8μ, and 14μ. Carbon tetrachloride has a very large absorption band at 13μ, which can not be confused with any of the small bands which are present.

The reflecting power being so low in all substances yet examined, except quartz and selenite, unless one has very sensitive measuring instruments, there is little hope of success in working out a calibration by means of bands of selective reflection.

Some gases, e. g., SO_2 and CO_2, have sharp absorption bands suitable for calibration work, but the accessory apparatus is not so easily manipulated as in the transmission of solids and liquids and in the emission from oxides.

WASHINGTON, May 16, 1911.

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International Metric System (chart).
Table of the Equivalents of Customary and Metric Weights and Measures.
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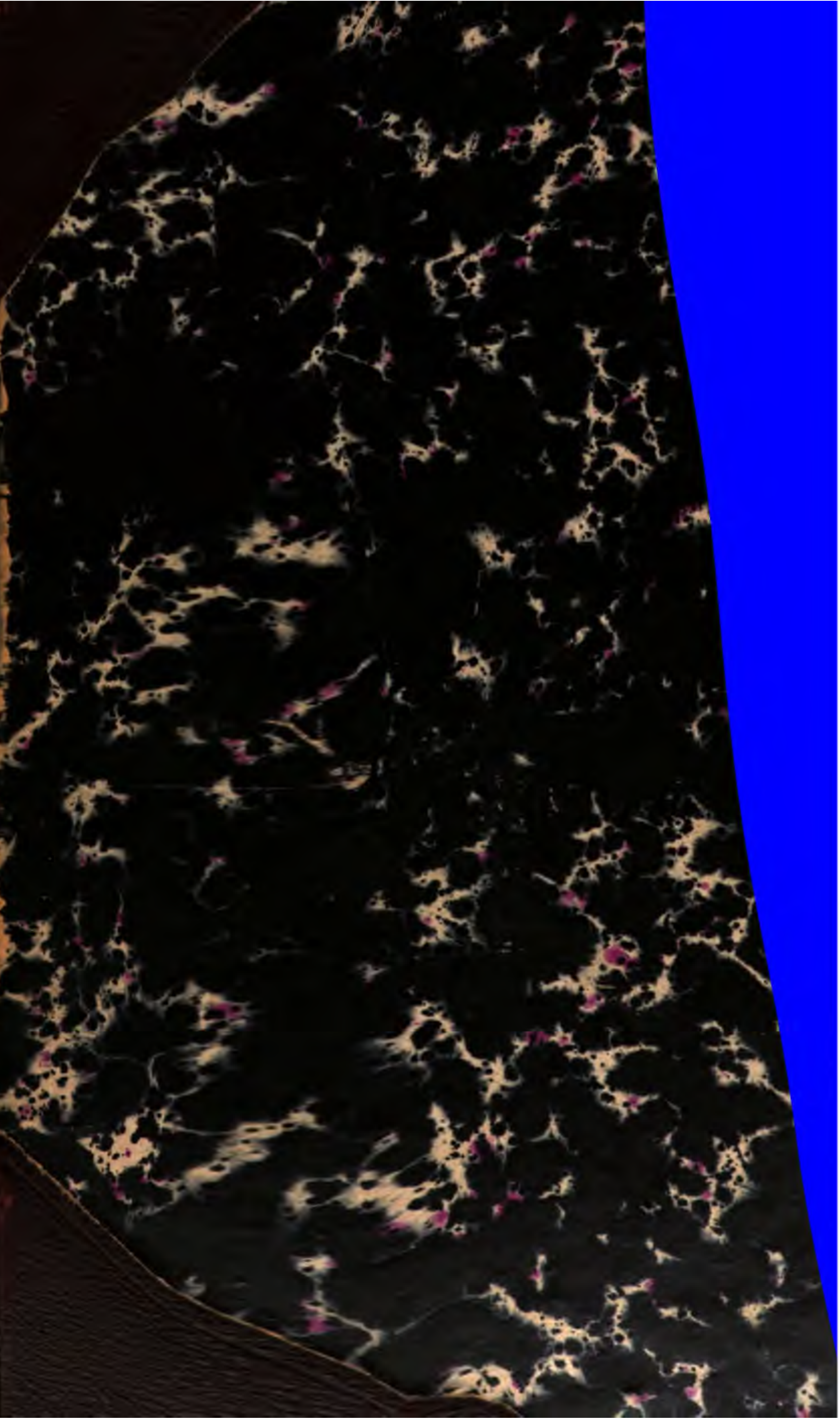

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